NASA CONTRACTOR REPORT

NASA CR-1791

NASA CR-1791

PREPARATION AND CHARACTERIZATION OF THE PYRRONES AS THERMAL STRUCTURAL MATERIALS

by B. G. Kimmel and L. E. Karre

Prepared by
HUGHES AIRCRAFT COMPANY
Culver City, Calif.
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1971

1. Report No. NASA CR-1791	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle PREPARATION AND CHARACTERIZATION OF THE PYRRONES AS THERMAL STRUCTURAL MATERIALS		5. Report Date September 1971 6. Performing Organization Code
7. Author(s) B. G. KIMMEL AND L. E. KARRE		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address HUGHES AIRCRAFT COMPANY AEROSPACE GROUP CULVER CITY, CALIFORNIA		11. Contract or Grant No. NAS1-7381 13. Type of Report and Period Covered CONTRACTOR REPORT
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D. C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

HIGH STRENGTH BLOWN AND SYNTACTIC FOAMS HAVE BEEN MADE FROM POLYIMIDAZOPYRROLONES (PYRRONE) WITH DENSITIES RANGING FROM 20 TO 60 POUNDS PER CUBIC FOOT. THE MONOMERS USED IN THE POLYMER SYNTHESIS WERE 3,3'-DIAMINOBENZIDINE AND 3,3',4,4'-BENZOPHENONE TETRACARBOXYLIC DIANHYDRIDE THAT WAS ESTERIFIED WITH EITHER ETHYL ALCOHOL OR ETHYLENE GLYCOL. BY CONTROLLING THE DEGREE OF ESTERIFICATION OF THE DIANHYDRIDE, A PREPOLYMER PRODUCT IS OBTAINED HAVING THE PROPER MELT FLOW CHARACTERISTICS AND CONTROLLED VOLATIVE GENERATION NECESSARY FOR THE PRODUCTION OF UNIFORM FOAMS. THIS PREPOLYMER IS MIXED WITH GLASS MICROBALLOONS OR A CHEMICAL BLOWING AGENT AND CURED IN A CLOSED MOLD TO FORM THE DESIRED FOAMED PRODUCTS. THE PROCEDURES FOR RESIN SYNTHESIS AND FOAM PRODUCTION ARE DESCRIBED AND THE PHYSICAL, MECHANICAL, AND THERMAL PROPERTIES OF THE PYRRONE FOAMS ARE DETAILED.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
PYRRONE POLYMERS, POLYIMIDAZOPYRROLONE, THERMAL STRUCTURAL FOAMS, PHYSICAL, MECHANICAL, THERMAL PROPERTIES	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
UNCLASSIFIED	Unclassified	97	$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

FOREWORD

This report was prepared by Hughes Aircraft Company to cover work performed under Contract NAS 1-7381 "Preparation and Characterization of the Pyrrones as Thermal Structural Materials." The work was administered by the Chemistry and Physics Branch, Langley Research Center, National Aeronautics and Space Administration, with Mr. Warren C. Kelliher as Project Engineer.

The program at Hughes was performed under the direction of Mr. Boyce G. Kimmel, Head, Plastics Research Group, Materials Technology Department, Research and Development Division. Dr. Leroy J. Miller directed the synthesis and chemical characterization of the polymer systems, and Mr. Lowell E. Karre was responsible for the development of the syntactic foam systems and the characterization of both the syntactic and the chemically blown systems.

The assistance of Mr. Ray E. Lawrence in chemical synthesis and Mr. W. Ken Johnson and Mr. Fred H. Smith in fabrication is gratefully acknowledged.

CONTENTS

ILLUSTRATIONS

TABLES

TABLES (Continued)

PREPARATION AND CHARACTERIZATION OF THE PYRRONES AS THERMAL STRUCTURAL MATERIALS

By B. G. Kimmel* and L. E. Karre*

1.0 SUMMARY

This report describes the development of techniques for preparing foams of various densities from the Pyrrone polymers which are formed by the condensation reaction of aromatic dianhydrides with aromatic tetraamines.

The work was divided into two principal phases: feasibility studies and the preparation and characterization of Pyrrone foams.

In the first phase, the feasibility of preparing foams from polymers formed by the condensation of 3, 3'-diaminobenzidine (DAB) with either pyromellitic dianhydride (PMDA) or 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride (BTDA) was investigated. Approaches used to prepare foams included the controlled heating of Pyrrone solutions, the use of volatile fillers, the addition of thermally activated chemical blowing agents, and the incorporation of lightweight fillers. From the results of the feasibility studies, the last two approaches, blowing agents and lightweight fillers, were chosen for further study and optimization. Although good foams were produced by the first two methods, heating of Pyrrone solutions and the use of volatile fillers, these methods were not felt to be adaptable to the fabrication of large foam sections. Also as a result of the feasibility studies, no further effort was expended on the nearly intractable PMDA-DAB polymers.

In the second phase, two types of Pyrrone foam were developed and characterized: a chemically blown foam and a syntactic foam. The initial goal of this effort was to produce foams of 30 and 60 pounds per cubic foot densities, but was later expanded to include production and

*Members of the Technical Staff, Materials Technology Department, Research and Development Division, Hughes Aircraft Company, Culver City, California.

characterization of the chemically blown and syntactic foams over the range of densities obtainable by these techniques. The characterization tests included the determination of the compressive and tensile strength over the temperature range from -100° to 700°F, thermal conductivity, and specific heat. The results of this characterization indicate that both types of Pyrrone foam show promise as thermal structural materials for aerospace applications.

2.0 INTRODUCTION

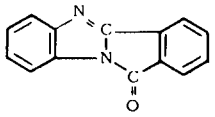
The Pyrrones (polyimidazopyrrolones), a new class of polymer developed at the NASA Langley Research Center, offer promise in present and future aerospace applications (reference 1). The ladder-like structures of these aromatic heterocyclic polymers have a greater proportion of aromatic cyclic groups than any other developmental polymer.

Pyrrones may be synthesized by the reaction of cyclic dianhydrides and tetraamines under comparatively simple reaction conditions. Depending on the starting materials, two basic structures can be obtained: the "stepladder" and the "ladder" polymers. In the stepladder form, the polyaromatic moieties are linked by single bonds. The ladder polymer is linked by double bonds at each end of the basic Pyrrone unit to form a continuous double strand polymer.

The principal objectives of this program are the development of processing techniques for the preparation of Pyrrone foams and their characterization as potential thermal structural materials. An implied objective is the preparation of Pyrrone prepolymers with sufficient tractability to allow subsequent processing into a cellular structure. The program was limited to the development and characterization of chemically blown foams and syntactic foams with 20 to 60 pounds per cubic foot densities from Pyrrones prepared by the reaction of 3,3'-diaminobenzidine with either 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA).

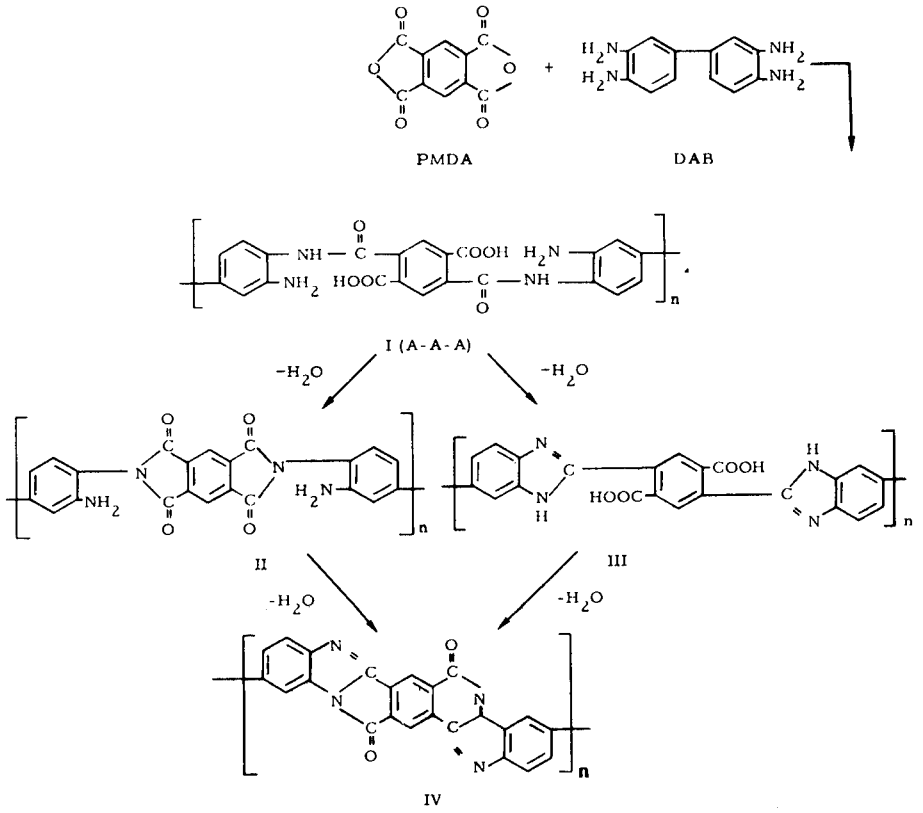
3.0 PYRRONE CHEMISTRY

The Pyrrones are a class of heterocyclic aromatic polymers having the following moiety as a recurring unit in the polymer chain:



This type of polymer was prepared by Bell and Pezdirtz under the name polyimidazopyrrolones or Pyrrone (references 2, 3, 4, 5). Other researchers in this field, including Dawans and Marvel, referred to these polymers as polybenzimidazolimides (reference 6) while Colson, Michel and Paufler (reference 7) referred to this class of polymers as polybenzoylenebenzimidazoles.

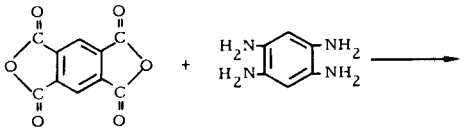
Pyrrones generally have been synthesized by the reaction of aromatic dianhydrides with aromatic tetraamines. The reactions are illustrated by the typical equations shown below for pyromellitic dianhydride (PMDA) and 3, 3'-diaminobenzidine (DAB).



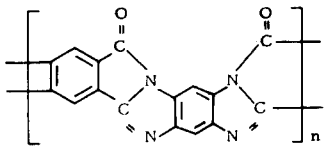
Several isomeric structures are possible for each of the indicated types of polymers. The initial reaction product (I) is a polyamide which undergoes two successive condensation reactions to form the Pyrrone structure (IV). Two main routes to the fully cyclized polymer are possible. Colson, Michel and Paufler found that the preferred route at temperatures between 130 - 150°C led to the formation of the polyimide (II), while others (references 3, 6) found evidence for the involvement of both polyimide and polybenzimidazole (III) intermediates.

Although the Pyrrone (IV) is insoluble, the amine-amide-acid (A-A-A) polymer (I) dissolves readily in such solvents as N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF), from which strong, but brittle, films can be cast. Cyclocondensation to convert (I) to (II) occurs at about 130 to 150°C in a film, and further condensation to form IV takes place above 200°C, with temperatures as high as 250°C required for complete conversion (reference 7).

One reason for the interest in Pyrrones is the possibility of forming ladder polymers, which theoretically should possess a considerable advantage over single-stranded polymers in terms of stability to radiation and heat. Such a ladder polymer can be formed (references 2, 3, 4, 6, 7) from pyromellitic dianhydride (PMDA) and 1, 2, 4, 5-tetraaminobenzene (TAB).



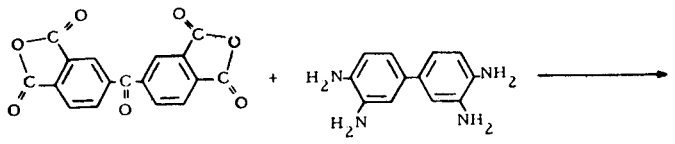
PMDA TAB



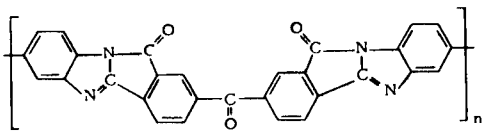
V

Most of the known Pyrrone polymers, however, have only a partial ladder structure and have been dubbed "stepladder" polymers (references 1, 2, 3, 4).

These polymers are exemplified by polymers (IV) and (VI), the latter being derived from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and DAB.

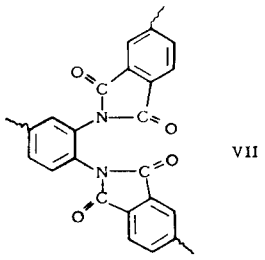


BTDA DAB

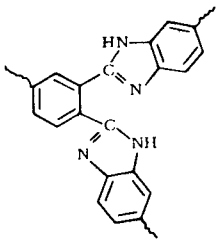


VI

The nature and extent of crosslinking may have a significant effect on the properties of the cured product. Simple crosslinks probably do not exist to a great extent, but a three-dimensional polymer can result from extensive branching. Two types of stable branching seem likely to be present, one involving imide linkages (VII) and the other having benzimidazole groups (VIII).



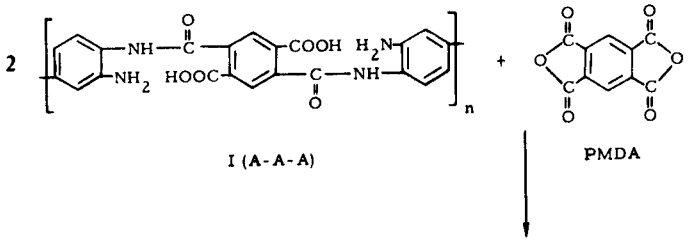
VII



VIII

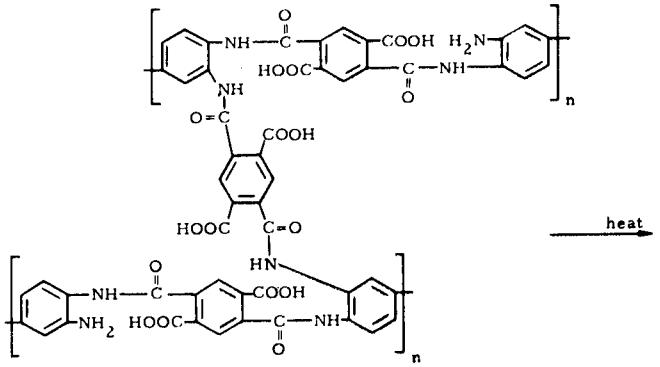
Gelation of the A-A-A polymer (I) occurs quickly in solution when a slight excess of dianhydride is added, but not when an excess of tetraamine is present (reference 7). Amide crosslinks (as shown in IX) are considered to be the cause of this gelation, since the amide

groups are formed only with anhydride and not with the much less reactive carboxyl groups. These crosslinks would appear to be conducive to the formation of imide branches or crosslinks of the type shown in (VII) and (X).

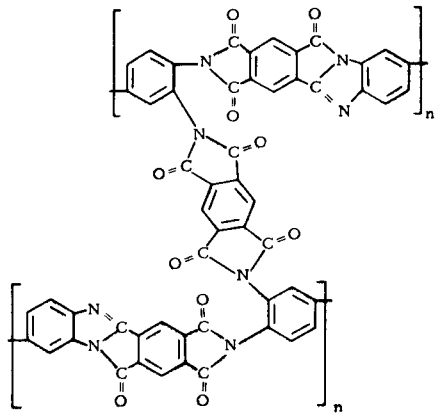


I (A-A-A)

PMDA



IX

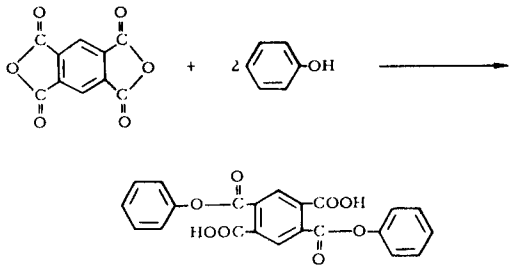


X

Using phthalic anhydride and o-phenylenediamine as model compounds, however, Dawans and Marvel found a tendency to form branches of the type indicated by (VIII) and reported none of the type shown in (VII).

Pyrrone polymerizations have been carried out both in a melt and in solution. Preferred solvents have been DMAc, DMF, dimethyl sulfoxide (DMSO), and polyphosphoric acid, but bis(2-methoxyethyl) ether (diglyme), phenol, and pyridine have also been used. Strong bonding between the polymer and the solvent (references 2, 3, 4) as well as between the polymer and moisture from the air (reference 5) has been noted. Interaction between the monomers and certain solvents is also likely.

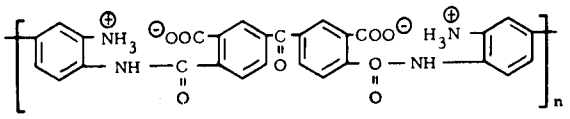
With few exceptions, the monomers always have been the dianhydride and the tetraamine or the tetraamine tetrahydrochloride. Bell and Jewell (reference 5) have reported using 2, 5-dicarbomethoxyterephthaloyl chloride in place of PMDA with no apparent change in polymer properties. Free tetracarboxylic acids were reacted with tetraamines to prepare polybenzimidazobenzophenanthrolines, a class of polymer which is related structurally to the Pyrrones (references 8, 9). Pyrrone synthesis in phenol (reference 4) almost certainly proceeds in part through phenyl ester intermediates, although this was not specifically mentioned in the report by Dawans and Marvel.



A prior interaction between the monomers and other solvents is also conceivable, and such reactions would alter the actual monomers.

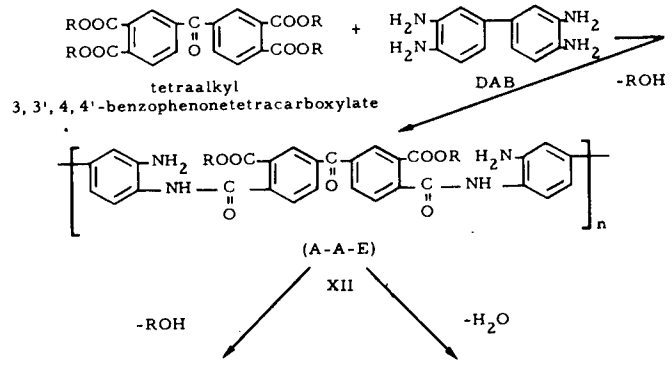
During initial work with these polymers in polar solvents such as DMAc and DMF, (references 10, 11) it was observed that the solvent free polymer was infusible and adequate flow could be obtained during cure only by allowing some solvent to remain in the polymer during processing.

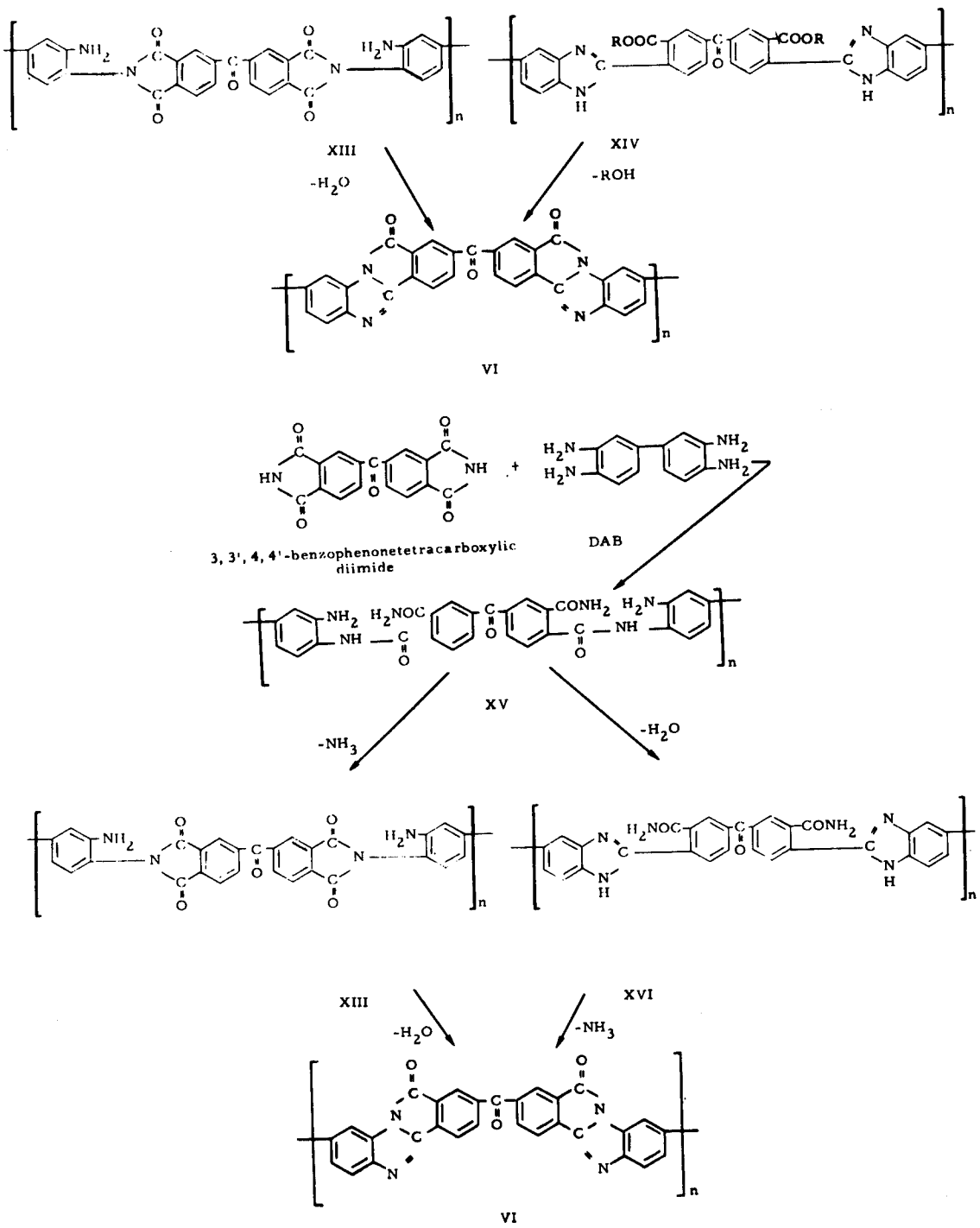
Infusibility of the polymer, which was actually the amine-amide-acid (A-A-A) polymer, was attributed to the strong electrostatic attractions between the ionic sites on the zwitterionic forms of the A-A-A polymer. For the A-A-A polymer derived from 3,3'4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzidine (DAB) this ionic structure is indicated by (XI).



XI

In order to avoid the formation of an ionic polymer it was decided to employ tetracarboxylic acid derivatives other than the dianhydrides. Esters and imides were suggested as being useful monomers for this purpose, the anticipated reactions follow.





Instead of the A-A-A polymer, the derivatives (XII and XV)of the A-A-A polymer are obtained, and the -COOH groups are replaced with the neutral -COOR or $-CONH_2$ groups. Both processes can produce the same polyimide (XIII) as that obtained by starting with the dianhydride, but different polybenzimidazole derivatives (XIV and XVI) are formed. Theoretically, all processes eventually lead to the same

Pyrrone (VI). However, none of the intermediates are ionic when the original monomer is either the diimide or the tetraester.

The nonionic character of the intermediates would be expected not only to improve the flow properties of the polymers during cure but to enhance their solubility in less polar solvents. Solvents less polar than DMAc should be more easily removed than DMAc, and the problem of hydrolysis of the bound DMAc could be avoided. Of the two possible nonionic intermediates (XII and XV), the amine-amide-ester (A-A-E) polymer (XII) was preferred since esters generally have lower melting points than amides.

Exploratory work at NASA-Langley Research Center indicated that improved Pyrrones could be obtained by preparing the polymers in ethylene glycol. Subsequent work at Hughes (references 10, 11) indicated that composities with improved mechanical strength properties could be developed with the ethylene glycol resin systems. Therefore, those resin systems formed through ethylene glycol ester intermediates were selected for use in the foam development program.

Initial studies involving oven foaming of the liquid resins met with only partial success. Although uniform, fine-celled foams were made by oven foaming, this method apparently could not be extended to preparing foams of relatively large dimensions. The emphasis was shifted from oven foaming these liquid resins to molding syntactic foams from resin powders obtained by precipitating the liquid resins in water. The initial evaluation of these ethylene glycol type resins is presented in Section 4. and subsequent work to develop syntactic foams in the density range from 30 to 60 pounds per cubic foot is presented in Section 6.

More recent research at Hughes (reference 11) revealed that the resins, formed from DAB and the ethyl alcohol esters of BTDA, showed mechanical strength values comparable to the BTDA-EG-DAB resins and thermal properties appreciably superior to the BTDA-EG-DAB resins. The initial evaluation of the BTDA-EtOH-DAB resin is presented in Section 4. and subsequent work to develop chemically blown foams in the density range from 15 to 45 pounds per cubic foot is presented in Section 5.

4.0 FEASIBILITY STUDIES

4.1 APPROACHES

Four approaches for preparing Pyrrone foams were considered sufficiently promising to warrant serious investigation. These were

A. Removal of solvent from a solution of the prepolymer by controlled oven heating to leave a cellular residue

B. Molding of a Pyrrone containing a suitable volatile filler and subsequent volatilization of the filler during postcure of the Pyrrone

C. Curing of a prepolymer containing a heat-sensitive, chemical blowing agent with a suitable decomposition temperature

D. The molding of a mixture of the prepolymer and a lightweight filler such as hollow glass spheres.

It was found (reference 11) that fine-celled, uniform Pyrrone foams could be prepared by the controlled oven heating of one type of Pyrrone resin. Specifically, Pyrrone prepolymers prepared in ethylene glycol from the diacid diester of the dianhydride and the tetramine produce foams when heated. This method seems to be equally applicable to Pyrrone prepolymers prepared from the reaction of DAB with either BTDA or PMDA.

The second method tried was a variation of one method for obtaining ceramic foams. In this method, a molding is prepared from a mixture of the prepolymer and a filler which will volatilize during the subsequent postcure to leave a porous structure. The relatively high postcure temperatures required to form the Pyrrone structure makes this method very attractive.

The success of the third method, producing a Pyrrone foam by the use of a thermally activated chemical blowing agent, depends on three main factors: (1) the use of a prepolymer with a controlled melting point range, (2) a satisfactory melt viscosity above the melting point and (3) a blowing agent with a decomposition temperature somewhat above the melting point of the prepolymer.

The fourth method is simple in principle – the molding of the correct proportions of prepolymer and a lightweight filler such as hollow glass bubbles to obtain a composite material of the desired density. Ideally, the finished molding should consist of uniformly distributed, unbroken bubbles in a voidfree cured polymeric matrix. On the one hand, the prepolymer should be sufficiently advanced to preclude the evolution of unduly large quantities of volatile reaction products during cure. On the other hand, if the prepolymer is advanced too far, excessively high curing pressures may be required which can result in a large fraction of broken bubbles. In the latter case, moldings of undesirably high density will be obtained. By the use of well chosen processing conditions, a fairly wide range of densities should be obtainable by this method. The upper density limit is that of the cured, unfilled, voidfree polymer, while the lower limit will also depend on the true density and the packing fraction of the glass bubbles.

4.1A OVEN HEATING OF PYRRONE PREPOLYMERS

Background

The first Pyrrone foam was prepared inadvertently during an attempt to coat a metal reed with BTDA-EG-DAB polymer for dynamic modulus measurements. The prepolymer used had been prepared in ethylene glycol solution by the reaction of DAB with the diacid diester of BTDA (reference 11). Examination of the polymer-coated reeds following measurement of the dynamic modulus revealed a dark colored, apparently void-free surface layer covering a yellow, foam-like material. Because of this unexpected result, a small quantity of the same prepolymer in ethylene glycol solution was heated for 4 hours at 300°F. A very uniform, fine-celled foam, with a density of approximately 33 pounds per cubic foot, was the result. Subsequent postcuring of this foam from 275° to 600°F yielded a hard, tough foam with a density of approximately 26 pounds per cubic foot. The foam apparently does not form by simple volatilization of the ethylene glycol. Usually, after about 20 minutes of

heating at 300°F, the prepolymer solution changes into a rubbery gel. The subsequent evaporation of the ethylene glycol then leaves a porous Pyrrone. Microscopic examination shows a fine, uniform, relatively open-celled structure with an average cell diameter of about 0.0015 inch. In appearance, the material resembles hard, brown leather.

Effect of Processing Conditions on Density of BTDA-EG-DAB Foams

A series of six BTDA-EG-DAB prepolymers was prepared using varying reaction times at reaction temperatures of 75° and 100°C. The BTDA was purified by heating overnight at 200°C in an argon atmosphere at ambient pressure. The DAB was used as received with no attempt at further purification. The ethylene glycol was purified by simple distillation under argon, with the fraction boiling in the range of 195°-197°C being collected.

Purified BTDA, 96.6 gm (0.3 mole), was dissolved in 150 ml of hot, purified ethylene glycol. The DAB solution was made by adding 64.2 gm (0.3 mole) of DAB to 325 ml of hot, purified ethylene glycol while stirring. The BTDA solution, heated to a specified temperature was added to the DAB solution at the same temperature while stirring. The resultant solution was then stirred for a specified period under argon.

A series of foams was made by oven heating at various temperatures small quantities of each of the BTDA-EG-DAB prepolymers made as described in the preceding paragraph. In each case, 25 gm of resin contained in an aluminum weighing dish was heated at the specified oven temperature for 16 hours. The resulting foams were postcured from 275° to 700°F over a period of 28 hours in an argon atmosphere. The density of each foam was measured before and after postcure. The results are summarized in Table I.

Both the synthesis conditions and the oven temperature markedly affect the final foam density of BTDA-EG-DAB foams obtained by this method.

Table I. Effect of Processing Conditions on Density of BTDA-EG-DAB Foams

Resin No.	Prepolymer Reaction Conditions		Oven Temperature °F	Density, lb/cu ft	
	Solution Temperature, °C	Mixing Time, minutes		Before Postcure	After Postcure
66A	75	15	275	38.9	23.8
			300	44.7	25.1
			325	36.6	34.6
			350	30.2	29.0
			375	27.1	25.2
			400	23.8	19.7
66B	75	60	275	43.8	22.0
			300	42.7	25.9
			325	31.5	29.8
			350	28.0	26.5
			375	21.6	19.4
			400	12.4	12.0
66C	75	240	275	32.1	21.5
			300	31.9	22.9
			325	29.0	27.1
			350	27.6	25.6
			375	23.8	22.7
			400	18.4	17.8
67A	100	5	275	44.7	23.9
			300	53.5	26.5
			325	32.2	30.6
			350	32.9	30.8
			375	32.8	25.4
			400	14.9	14.1
67B	100	20	275	34.0	24.1
			300	35.3	24.4
			325	33.5	31.4
			350	30.0	28.0
			375	27.3	25.7
			400	17.4	16.8
67C	100	35	275	21.3	19.3
			300	21.1	19.8
			325	*	*
			350	*	*
			375	18.3	17.4
			400	19.1	18.3

*Specimen broke. Density not determined.

Effect of Processing Conditions on Density of PMDA-EG-DAB Foams

The oven foaming of BTDA-EG-DAB prepolymers described in the previous section was repeated on a series of PMDA-EG-DAB prepolymers. Varying reaction times at temperatures of 75° and 100°C were used. The PMDA was purified by vacuum sublimation in the temperature range of 205°-220°C. The DAB was used as received. The ethylene glycol was purified by simple distillation under argon, with the fraction boiling in the range of 195°-197°C being collected.

Purified PMDA, 87.3 gm (0.4 mole), was dissolved in 100 ml of hot, purified ethylene glycol. The DAB solution was made by adding 85.7 gm (0.4 mole) of DAB to 365 ml of hot, purified ethylene glycol while stirring. The PMDA solution, heated to a specified temperature, was added to the DAB solution at the same temperature while stirring. The resultant solution was then stirred under argon for a specified period.

A series of foams was made by oven heating at various temperatures small quantities of each of the PMDA-EG-DAB prepolymers using the same procedure as used for the BTDA-EG-DAB prepolymers. As before, the density of each foam was measured before and after a postcure in argon to 700°F. The results are summarized in Table II.

Good foams with densities ranging from 19 to 27 pounds per cubic foot were obtained at oven temperatures of 275° to 325°F. Foams of somewhat poorer quality with densities from 15 to 21 pounds per cubic foot were obtained at higher temperatures. In general, the foams prepared at higher temperatures showed a tendency to crack.

Compressive Strength Properties of BTDA-EG-DAB Foam

A block of foam measuring approximately 3 x 3 x 3 inches was made by oven heating a BTDA-EG-DAB (diacid diester) resin for 40 hours at 350°F. The resulting foam was extremely hard and strong although a few shrinkage cracks were evident. Postcuring from 300° to 850°F over a period of 57 hours and an additional 1-1/2 hours at

Table II. Effect of Processing Conditions on Density of PMDA-EG-DAB Foams

Resin No.	Prepolymer Reaction Conditions		Oven Temperature °C	Density, lb/cu ft	
	Solution Temperature, °C	Mixing Time, minutes		Before Postcure	After Postcure
69AR	75	15	275	48.7	22.8
			300	49.0	24.7
			325	39.8	25.2
			350	18.2	17.5
			375	*	*
			400	20.1	18.7
69B	75	60	275	45.6	22.5
			300	42.6	22.8
			325	32.8	23.6
			350	23.0	21.3
			375	20.9	19.6
			400	20.4	19.8
69C	75	180	275	49.4	20.9
			300	38.6	21.8
			325	29.5	21.1
			350	20.2	19.3
			375	20.0	19.2
			400	18.8	19.5
69E	100	5	275	47.6	23.3
			300	38.1	23.4
			325	35.3	25.8
			350	18.7	17.7
			375	*	*
			400	19.6	18.1
69F	100	30	275	59.7	27.6
			300	47.8	26.9
			325	34.5	26.8
			350	*	*
			375	*	*
			400	*	*
69G	100	60	275	58.1	21.8
			300	42.1	18.9
			325	40.8	18.8
			350	20.9	18.8
			375	19.3	17.4
			400	17.4	14.9

*Sample broken or irregular. Density not determined.

850° F resulted in the formation of several large cracks. Aside from the cracked areas, the surface was uniform in appearance. The post-cure darkened the specimen from yellow to dark brown. The density was much higher than those densities previously obtained in preparing small specimens.

Compressive specimens, 3/8 inch in diameter by 3/4 inch long were machined from the block in two directions: the "A" direction, with its axis parallel to the vertical direction of the block as foamed and the "B" direction, with the axis perpendicular to that of the "A" specimens.

The compressive yield strength, ultimate compressive strength, and modulus in compression were determined in accordance with ASTM D695 from compressive tests run at room temperature. Although the scatter in the results indicated some non-uniformity in the specimens, the initial results were quite encouraging. Ultimate compressive strength values in excess of 2000 psi were obtained in both and A and B directions. No real difference in the compressive strength or yield strength of the A and B directions is apparent. However, the compressive modulus of the B specimens is significantly higher than that of the A specimens. Prior to making the compressive strength measurements, the density of each specimen was calculated from weight and volume measurements. The results are summarized in Table III.

Conclusions

Oven heating can be used to make very fine-celled foams from ethylene glycol solutions of Pyrrone prepolymers prepared from the diacid-diester of the anhydride and DAB. By the use of certain combinations of synthesis conditions and oven temperature, BTDA-EG-DAB foams with a nominal density of 30 pounds per cubic foot can be made. Other processing conditions can be used to obtain BTDA-EG-DAB foams with lower densities in the range of 12-25 pounds per cubic foot. PMDA-EG-DAB foams can also be obtained by this process, but with densities in the range of 20-25 pounds per cubic foot.

Table III. Compressive Properties of BTDA-EG-DAB Foam

Specimen Type	Specimen Number	Density, lb/cu ft	Ultimate Comp. Strength, psi	Comp. Yield Strength, psi	Modulus in 10^5 psi
A	1	41.3	265*	-	-
	2	40.7	2155	1200	1.41
	3	39.9	2410	2300	1.11
	4	34.7	1610	1610	0.97
Averages			2060	1700	1.16
B	1	37.6	2430	1990	1.61
	2	33.9	1480	1390	1.42
	3	36.6	1775	1450	2.07
	4	35.0	1220	950	2.08
Averages			1730	1440	1.80

*Not included in average

The success of this method is highly size dependent. Small discs of BTDA-DAB foam with a nominal density of 30 pounds per cubic foot can be made readily by this method. Attempts to make larger blocks by this method were unsuccessful. The final, postcured density was significantly higher (35-45 pounds per cubic foot) for larger billets of foam. In addition, the larger billets showed a tendency to crack and warp during cure and postcure.

Although modification of the processing conditions might result in some improvement, the prospects of making relatively large sections of foam by this method are far from promising. Therefore this method was not pursued further.

4.1B VOLATILE FILLERS

Discussion

One method used successfully in the preparation of ceramic foams involves extruding or otherwise forming the ceramic composition containing a readily volatilized filler such as powdered polymethylmethacrylate. Prior to the final firing, the filler is volatilized by a carefully controlled heating cycle. This method was felt to show promise for two reasons. The inherent heat stability of the Pyrrone polymers implied that such a method might be applicable to the Pyrrones. It would be expected that the density and cell structure of the resultant materials could be very closely controlled by the amount and particle size distribution of the volatile filler used. The heating cycle required to volatilize the filler can also serve to postcure the molding to final polymeric form. One possible drawback to this method would be its applicability to the fabrication of relatively large sections which would involve the volatilization of relatively large quantities of filler from a relatively small surface area.

Screening of Fillers

Several thermoplastic molding materials were checked as potential volatile fillers by oven heating small quantities at 700° F. This temperature was chosen as being a reasonable maximum postcure temperature for Pyrrones. The plastics evaluated included methyl methacrylate polymer (acrylic), polyacetal, polyethylene, vinyl acetate, and polystyrene. The acrylic cleanly decomposed to the monomer after 10 minutes at 700° F, leaving no residue. The other plastics darkened and partially decomposed but did not volatilize after several hours at 700° F.

Based on the foregoing results, it was concluded that powdered acrylic should be tried as a volatile filler in combination with powdered prepolymers.

Preparation of Foams

The first molding was prepared from a mixture of 67 percent of precipitated, dried BTDA-DAB Pyrrone (made from the diacid-diester of BTDA with ethylene glycol)and 33 percent of finely powdered acrylic. A 3/4-inch diameter by 1 inch thick disc was molded by applying a pressure of 10, 000 psi at 300° F for one hour. The resultant molding was of uniform appearance and medium brown in color. Postcuring in air from 275° to 700° F over a period of 28 hours apparently volatilized the acrylic completely leaving a fine-celled Pyrrone foam with a density of 37 pounds per cubic foot. This foam was somewhat friable in nature which might be attributable to either air oxidation during postcure or to poor flow of the Pyrrone prepolymer during molding.

A second attempt to prepare a foam by this method was far more successful. A very uniform, apparently strong foam was made by postcuring a disc molded from a mixture of 67 percent of a BTDA-EtOH-DAB prepolymer and 33 percent of finely powdered acrylic. The thoroughly blended mixture was placed in a 1-1/8 inch diameter mold at room temperature and subjected to a pressure of 10, 000 psi. The temperature was increased from room temperature to 275° F, held at 275° F for 5 hours, increased to 500° F over a period of 5 hours and cooled to below 200° F. The resulting molding was dark brown, uniform in appearance and had a density of 66. 3 pounds per cubic foot. Postcuring from 275° to 700° F in argon seemed to effect complete volatilization of the acrylic to give a cellular Pyrrone with a density of 38. 3 pounds per cubic foot. The cell structure was remarkably fine and uniform (see Figure 1 for typical cross section). Most cells were in the range of 0. 002-0. 004 inch with a few cells as large as 0. 007 inch.

A formulation of 53 percent BTDA-EtOH-DAB prepolymer and 47 percent acrylic was calculated to give a postcured density of 30 pounds per cubic foot making allowance for the weight loss and shrinkage of the Pyrrone during postcure. A molding of this composition yielded a foam with a density of almost exactly 30 pounds per cubic foot when postcured in argon to 700° F.

Several unsuccessful attempts were made to prepare foams with higher densities up to 60 pounds per cubic foot by the incorporation of smaller quantities of acrylic. Pure BTDA-EtOH-DAB prepolymer and formulations containing 2, 5 and 10 percent acrylic were molded. In all cases, the cured moldings contained many fine cracks some of which extended through the depth of the specimen.

Figure 1. Cross-Section of Pyrrone Foam Made by Volatile Filler Process (20X)

Attempts to prepare a larger piece of foam by the volatilization of a filler during postcure were unsuccessful. A disc 1 inch thick by 2-1/4 inches in diameter was molded from a formulation containing 47 percent acrylic. The molded disc was very uniform in appearance and had a density of 68.5 pounds per cubic foot. Half of the disc was postcured from 300° to 700°F over a period of 5 days while the other was postcured over the same temperature range over a period of 10 days. Both halves were extensively cracked after postcure. In addition, it was apparent that the acrylic filler had incompletely volatilized during postcure.

In spite of the incomplete removal of the acrylic and the cracking, the cell structure of the resulting foams was extremely fine and uniform. The results obtained serve to confirm that, as anticipated, the postcure of Pyrrone-acrylic moldings becomes increasingly difficult, with increasing size.

Compressive Strength Properties

The compressive properties at room temperature were determined on the Pyrrone foams with densities of 30 and 38.3 pounds per cubic foot. The compressive strength properties of the 38.3-pound foam were approximately twice as high as those of the 30-pound foam. Table IV which follows gives the complete results.

Table IV. Compressive Strength Properties of BTDA-DAB Foams made by Volatile Filler Process

Density, lb/cu ft	Ult. Compressive Strength, psi	Compressive Yield* Strength, psi	Modulus In 10^5 psi
38.3	5210	1530	1.97
	5600	1990	2.04
Averages	5405	1760	2.00
30.0	2360	1000	1.53
	2810	860	1.43
Averages	2585	930	1.48

*Compressive Stress at Proportional Limit

Conclusions

Strong, uniform, fine-celled Pyrrone foams with closely controlled density can be made by the controlled postcure of Pyrrone moldings containing a volatile filler such as finely powdered acrylic. Unfortunately, it becomes increasingly difficult to volatilize the filler during postcure as the size of the moldings is increased. Therefore this method of producing a cellular Pyrrone is probably not suitable for the production of relatively large sections of foam.

4.1C CHEMICAL BLOWING AGENTS

Discussion

The most straightforward method of preparing a virtually pure plastic foam involves the use of a thermally activated chemical blowing agent. The success of this method is dependent on the controlled decomposition of the blowing agent, accompanied by the liberation of a gas at a temperature where the plastic exists in the form of a viscous melt. The viscosity of the melt during decomposition of the blowing agent must be sufficiently high to retain the liberated gas. On the other hand, if the melt viscosity is too high, excessive internal pressures may result in cracking or fracturing of the foamed structures.

Prepolymers prepared from DAB and the tetraethyl ester of BTDA were felt to be an excellent choice due to their relatively low melting point (120°-130°C). Prepolymers of this type would be expected to foam naturally upon application of heat, due to the evolution of ethyl alcohol of reaction. Thus it might be possible to prepare foamed Pyrrone polymers without the addition of a chemical blowing agent.

Powdered prepolymers obtained by precipitation from ethylene glycol solutions were also considered in preparing chemically blown foams. However, these materials have widely varying (or non-existent) melting points. To some extent, the melting point appears to be dependent on the precipitation procedure used and the resultant amount of residual glycol in the precipitated, dried prepolymer.

Initial Foaming Experiments

The first chemical foaming experiments involved the heating of mixtures of a precipitated, powdered prepolymer, blowing agent and a surfactant in a small aluminum cup contained in a temperature controlled heating block.

The most promising foam was obtained initially by heating a mixture of 5 gm of precipitated BTDA-EG-DAB prepolymer (tetraester type), 0.05 gm of Celogen AZ*, and one drop of Silicone L-521** added as a surfactant. The mixture started melting at 291°F. At 410°F, the mixture was completely melted and at 428°F, foaming proceeded smoothly. The resultant foam was hard and tough, though rather large-celled, and had a density of 18.3 pounds per cubic foot.

Further attempts to produce foams with densities of 30 and 60 pounds per cubic foot involved heating the prepolymer blowing agent-surfactant mixture in a closed mold. This procedure was felt to be necessary in order to control the density within reasonably close limits. Several mixtures were formulated from a precipitated prepolymer prepared from another batch of BTDA-EG-DAB resin. The quantity of blowing agent (either Celogen AZ or Celogen RA***) was varied from 0.5 to 2.0 percent. Regardless of the amount of blowing agent used, the mixture did not foam completely. Melting point tests run on the pure prepolymer indicated that it did not actually melt on heating, but merely softened and fused. There was a strong indication that the precipitation procedure significantly affected the amount of residual ethylene glycol in the precipitated Pyrrone. This residual glycol in turn affected the foaming characteristics. Those prepolymers which contained relatively little residual glycol had no detectable melting point and did not form foams when heated with a blowing agent.

BTDA-EtOH-DAB prepolymers as synthesized by a melt polymerization process are solid materials with a well defined melting point in the range of 120°-130°C. It was felt that a prepolymer of this type combined with a suitable blowing agent and properly heated should yield a Pyrrone foam. The addition of a blowing agent might not be necessary since the ethyl alcohol of reaction in the form of a gas might act as a blowing agent.

---

*Naugatuck Chemical (decomposition temperature, 350°F)
**Silicones Division, Union Carbide
***Naugatuck Chemical (decomposition temperatures, 415° -435°F)

Initial attempts to prepare a foam from the BTDA-EtOH-DAB prepolymer were not successful. Some foams prepared by heating prepolymer-blowing agent mixtures in an open cup were low density (about 11 pounds per cubic foot) and friable. Others had a non-uniform cell structure caused by partial collapse of the foam before complete hardening of the resin. It was evident that prepolymers of the BTDA-EtOH-DAB type could be used in preparing chemically blown foams only if the proper curing cycle were chosen.

Several additional series of chemically blown foams were made by oven heating mixtures of BTDA-EtOH-DAB prepolymer and either Celogen OT (decomposition temperature, 266° F) or Celogen AZ (decomposition temperature, 350° F). The first foams were made by free foaming mixtures in an oven at 350° F and finally curing at 400° F. Both blowing agents were used in concentrations of 0.5 and 1.0 percent. Strong foams were obtained, but in all cases the cell size was large, ranging from 1/16 to 3/16 inch in diameter. Foams were then made using the Celogen OT as a blowing agent and with the oven temperature reduced to 275° F. Foams of fair quality with finer cells and with densities in the range of 22-24 pounds per cubic foot resulted. The foams made at 275° F were extremely fragile until postcured for at least 2 hours at 400° F.

Attempts were then made to increase the foam density by heating mixtures containing successively smaller amounts of Celogen OT blowing agent. Mixtures containing, respectively, 0.25, 0.12, 0.06 and 0.0 percent blowing agent all yielded foams with densities in the range of 22-24 pound cubic foot. This indicated the foaming observed was largely due to the evolution of volatiles during heating.

Since satisfactory foams in either a 30 or 60 pound density could not be obtained by the free foaming technique, heating the mixtures in a closed mold was initiated. By this technique, the correct quantity of powdered foamant is placed in a mold. The material is then preformed by the application of pressure. The top punch is then withdrawn partially and a steel shim (or land) of the correct thickness is inserted to establish a mold volume calculated to yield a foam of the required

density. Heating of BTDA-EtOH-DAB prepolymer-Celogen OT mixtures at 275°F was shown to yield foams with a fine uniform cell structure (see Figures 2 and 3). A further programmed cure up to 500°F was found to be necessary to give foams which were not fragile and friable. The curing conditions finally adopted as standard in preparing chemically blown foams were the following: the mold containing the foaming mixture is placed in a cold oven; the oven temperature is increased to 275°F over a period of approximately 20 minutes, the temperature is maintained at 275°F for 5 hours and then increased from 275° to 500°F over a period of 5 hours.

The presence of a small quantity of Celogen OT was found to be essential in making fine-celled, uniform foams in a closed mold. Foams prepared from the pure prepolymer were relatively coarse and not nearly so uniform as those prepared from mixtures containing the blowing agent.

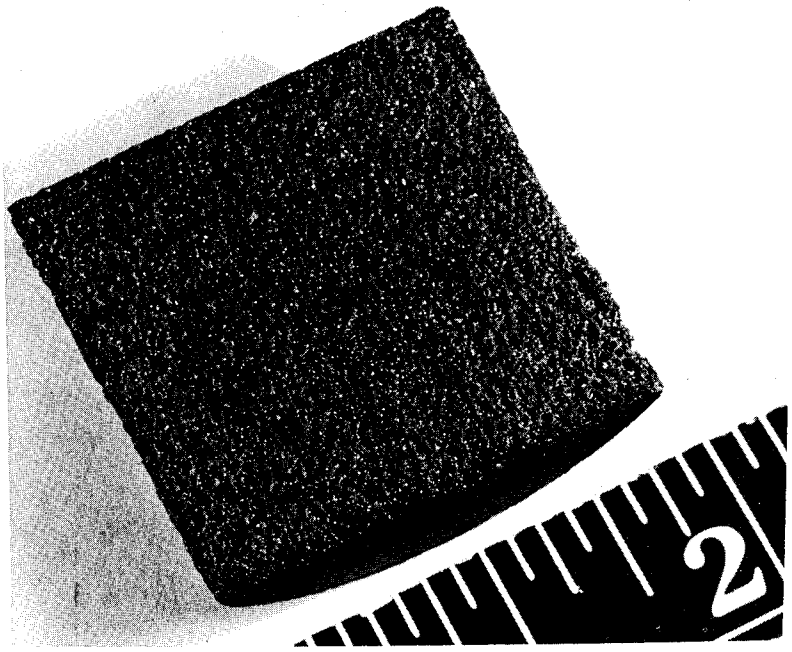


Figure 2. Cross-Section of Chemically Blown Pyrrone Foam

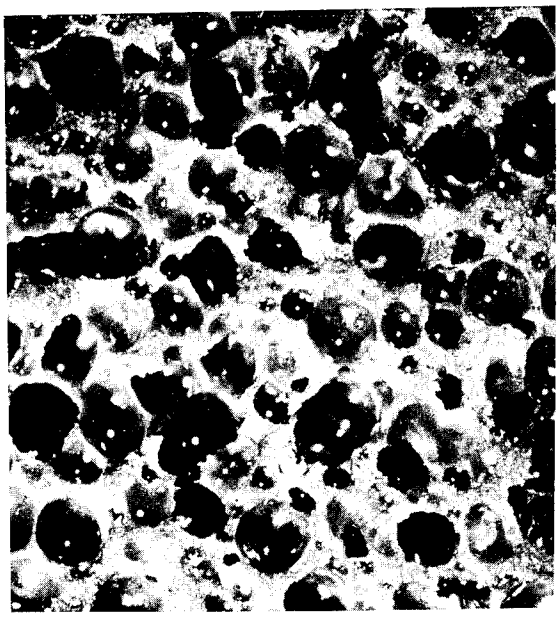


Figure 3. Cell Structure of Chemically Blown Pyrrone Foam (20X)

Since high shrinkage (approximately 20 volume-percent) occurs during curing, some foam moldings were found to have one or more large shrinkage cracks in the center. These cracks were apparently caused by a combination of curing shrinkage and the molding sticking to the sides of the mold. In other words, the material literally shrank away from itself. This problem was completely eliminated by coating the inside of the mold with a thin layer of polytetrafluorethylene.

The method of mixing the prepolymer and blowing agent was found to affect markedly the quality and uniformity of the resulting foam. Initially, mixtures were prepared by simple grinding in a mortar and pestle. The foams made from mixtures compounded in this way were inconsistent in quality and very often contained large bubbles.

Intimately blended mixtures were obtained by mixing the ingredients in a high shear blender along with an inert liquid which acts as a suspension medium. Since this liquid must be removed subsequently by filtration and drying, it should be relatively volatile. One liquid

which met the above requirements in addition to being non-toxic and non-flammable was Freon TF*. Excellent foams with cell sizes in the range of 0.008-0.020 inch were prepared from mixtures prepared with the aid of this compound. Figure 4 shows plainly the pronounced difference in foam quality obtained by the two mixing methods.

Effect of Postcure on BTDA-EtOH-DAB Foam

A block of BTDA-EtOH-DAB foam with a nominal density of 30 pounds per cubic foot was taken for the postcure study. Thirty-six half-inch diameter, 1 inch long cylindrical specimens were machined from

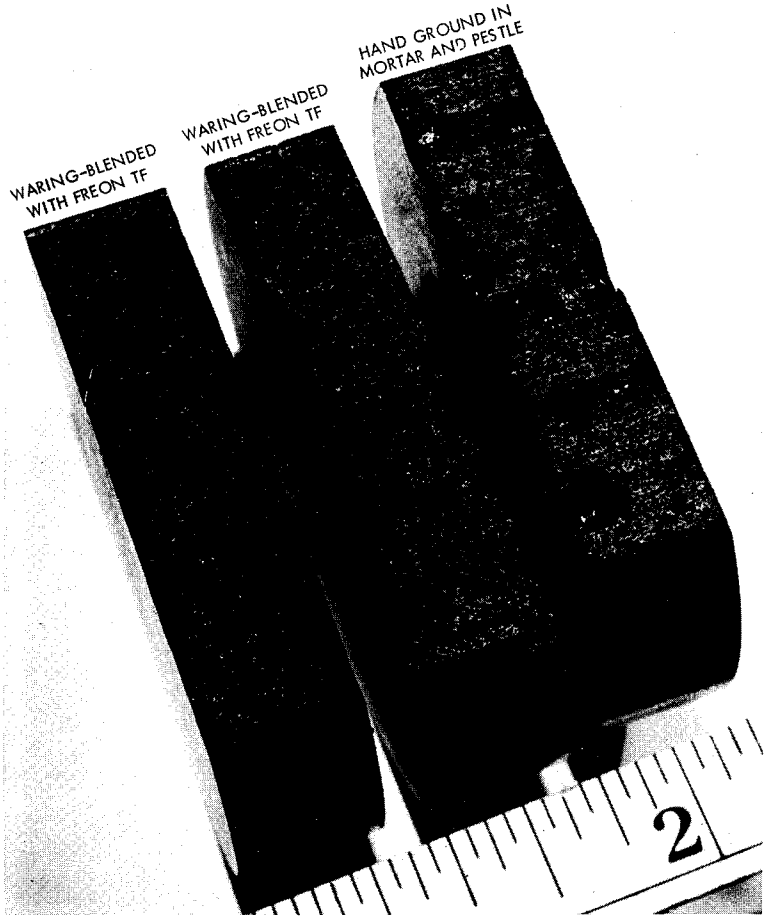


Figure 4. Effect of Mixing Method on Uniformity of Pyrrone Foams

*DuPont's trichlorotrifluoroethane.

the block with the axes perpendicular to the 4-1/2 x 6-1/2 inch faces. The specimens were randomly divided into six sets of six specimens each and were assigned to the following postcure cycles conducted in argon with a rate of temperature rise of 25° F/hour.

No. 1 Room temperature to 500° F
No. 2 Room temperature to 600° F
No. 3 Room temperature to 700° F
No. 4 Room temperature to 800° F
No. 5 Room temperature to 850° F
No. 6 Room temperature to 850° F, plus one hour at 850° F.

After identifying, weighing and measuring individual specimens, each set of six specimens was sealed in a small stainless steel bag equipped with a tube to admit argon and a small vent. All of the steel bags were connected to an argon cylinder by means of a manifold. The sealed bags were placed in a large, forced draft oven equipped with an accurate programming controller. Each bag was removed at the appropriate point in the postcure cycle. Individual specimens were again weighed and measured. The effect of each postcure on the weight, dimensions and resultant density of each specimen was calculated. The results are shown in Table V.

Table V shows that both the weight loss and shrinkage are significantly affected by the type of postcure. Continued weight loss and shrinkage are observed at 850° F. The end result is a moderate decrease (0.3-0.7 pounds per cubic foot) in the density as a result of postcure. The postcuring shrinkage is in addition to a very high molding shrinkage of approximately 18 volume-percent. Thus, for a postcure to 700° F (Postcure No. 3), the total shrinkage, based on the original mold volume, is approximately 30 volume-percent.

Despite this relatively large shrinkage, little or no warpage occurs either during the molding process or the postcuring cycle.

Table V. Effect of Postcure Conditions on Weight, Dimensions and Density of BTDA-EtOH-DAB Foams

Property	Specimen Number	Postcure Cycle					
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Weight Loss, Percent	1	2.4	7.1	15.6	19.1	21.1	22.0
	2	2.2	6.8	15.4	19.2	22.2	22.4
	3	2.6	6.6	15.5	19.1	21.2	22.6
	4	2.5	6.8	15.2	18.9	20.6	22.0
	5	2.4	6.6	15.7	19.2	21.8	22.1
	6	2.6	6.8	15.5	19.0	20.4	22.0
Average		2.4	6.8	15.5	19.1	21.2	22.2
Decrease in Diameter, Percent	1	0.0	2.0	4.9	5.9	7.5	7.3
	2	0.4	2.0	5.1	6.1	6.9	7.3
	3	0.4	1.8	5.1	6.1	7.3	7.5
	4	0.4	2.0	4.9	6.1	6.9	7.5
	5	0.4	2.0	5.1	5.9	7.1	7.5
	6	0.6	2.0	5.1	6.1	7.1	7.5
Average		0.4	2.0	5.0	6.0	7.1	7.4
Decrease in Thickness, Percent	1	0.5	2.0	4.9	5.9	6.6	7.2
	2	0.4	1.9	4.9	6.0	6.9	7.5
	3	0.5	1.8	4.8	6.1	7.0	7.3
	4	0.5	2.0	4.8	5.7	6.8	7.2
	5	0.5	1.9	4.9	6.0	7.0	7.3
	6	0.6	2.0	4.8	5.9	6.9	7.6
Average		0.5	1.9	4.8	5.9	6.9	7.4

Table V. Effect of Postcure Conditions on Weight, Dimensions and Density of BTDA-EtOH-DAB Foams (Continued)

Property	Specimen Number	Postcure Cycle					
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Decrease in Volume, Percent *	1	0.4	5.9	14.0	16.8	20.0	20.4
	2	1.2	5.8	14.3	17.2	19.3	20.4
	3	1.2	5.1	14.1	17.3	20.1	20.8
	4	1.3	5.6	14.0	16.8	19.1	20.7
	5	1.4	5.7	14.5	17.0	19.9	20.5
	6	2.0	5.7	14.4	17.0	19.9	21.2
Average		1.2	5.6	14.2	17.0	19.7	20.7
Density Before Postcure, lb/cu ft	1	30.5	30.4	32.2	28.1	27.9	29.4
	2	28.7	30.7	30.5	33.0	31.5	31.7
	3	30.3	31.3	30.4	32.4	31.8	29.9
	4	31.7	30.3	34.7	31.6	27.2	30.6
	5	30.5	30.2	29.6	30.6	29.0	30.5
	6	32.1	29.0	31.8	32.3	31.2	28.7
Average		30.6	30.3	31.5	31.3	29.8	30.1
Density After Postcure, lb/cu ft	1	29.9	30.0	31.6	27.3	27.5	28.8
	2	28.4	30.4	30.1	32.2	30.4	30.9
	3	29.9	30.8	29.8	31.7	31.2	29.2
	4	31.3	29.9	34.2	30.8	26.7	30.1
	5	30.2	29.9	29.2	29.8	28.3	29.9
	6	31.9	28.8	31.4	31.5	31.0	28.4
Average		30.3	30.0	31.0	30.6	29.2	29.6
Decrease in Aver. Density, Percent		1.0	1.0	1.6	2.2	2.0	1.7

*Calculated from expression, (1 - Wa Db/Wb Da x 100), where Wb and Wa equal weights before and after postcure, respectively, and Db and Da equal densities before and after postcure, respectively.

The compressive strength properties of the variously postcured BTDA-EtOH-DAB foams were determined. The compressive yield strength and modulus in compression were determined at room temperature while the ultimate compressive strength was determined at room temperature and 600° F. The complete test results are given in Table VI.

Despite a fairly large spread in the individual test values, several conclusions can be drawn from the data. The room temperature ultimate compressive strength values are the highest (approximately 3000 psi) for postcure temperatures of 600° and 700° F. The compressive strength at 600° F is virtually unaffected by postcure temperature with the possible exception of 850° F. The postcure temperature has no significant effect on the compressive yield strength or modulus, probably due to the large spread in individual values for these properties.

Based on the effect of postcure on shrinkage and room temperature compressive strength, a postcure to a maximum temperature of 700° F was adopted as being reasonable. Upon postcuring to 700° F, no serious degradation of compressive strength occurs as observed after postcuring to 800° F and higher. On the other hand, the shrinkage observed upon postcuring to 700° F is approximately 2-1/2 times as high as that observed as a result of a 600° F postcure.

Chemically Blown PMDA-EtOH-DAB Foams

An attempt was made to prepare a 30-pound foam from a PMDA-EtOH-DAB prepolymer. The general procedure was the same as used in the preparation of the BTDA-EtOH-DAB foams except that Celogen AZ (decomposition temperature, 350° F) was used instead of Celogen OT (decomposition temperature, 266° F). In addition, the mold was heated initially to 350° F instead of 275° F to allow for the higher decomposition temperature of the blowing agent.

Table VI. Effect of Postcure Conditions on Compressive Strength Properties of BTDA-EtOH-DAB Foams

Postcure Cycle	Compressive Strength, psi		Compressive Yield Strength at Room Temperature, psi	Modulus at Room Temperature in 10^5 psi
	Room Temperature	600° F		
No. 1 (500° F)	1740 (29.9) 2200 (28.4) 2110 (29.9)	1520 (31.3) 980 (30.2) 1540 (31.9)	1130 650 680	2.83 1.62 1.70
Averages	2020	1350	820	2.05
No. 2 (600° F)	3540 (30.0) 3170 (30.4) 2390 (30.8)	1070 (29.9) 1310 (29.9) 1990 (28.8)	1230 750 850	3.08 1.87 2.12
Averages	3030	1460	940	2.36
No. 3 (700° F)	3570 (31.6) 2370 (30.1) 3370 (29.8)	1710 (34.2) 1560 (29.2) 1240 (31.4)	1580 -- 590	3.94 -- 1.48
Averages	3100	1500	1080	2.71
No. 4 (800° F)	1920 (27.3) 1710 (32.2) 1690 (31.7)	1220 (30.8) 1650 (29.8) 1170 (31.5)	820 1180 1250	2.04 2.95 3.12
Averages	1770	1350	1080	2.70
No. 5 (850° F)	1600 (27.5) 2630 (30.4) 1480 (31.2)	1320 (26.7) 1700 (28.3) 1600 (31.0)	750 1420 790	3.75 3.56 1.98
Averages	1900	1540	990	3.10
No. 6 (850° F + 1 hr soak)	2240 (28.8) 1290 (30.9) 2520 (29.2)	870 (30.1) 1070 (29.9) 1090 (28.4)	730 990 950	1.81 2.47 2.38
Averages	2020	1010	890	2.22

Note: Figures in parentheses are the densities in pounds per cubic foot of individual test specimens.

The resulting molding had a density of 60 pounds per cubic foot and, examined microscopically, was seen to be a porous, open-celled, partially compacted material rather than a closed-cell foam. Apparently, the prepolymer did not actually fuse at any point in the molding process.

Another unsuccessful attempt was made to prepare a chemically blown foam using a much less advanced PMDA-EtOH-DAB prepolymer. Again, a porous molding with a nominal density of 60 pounds per cubic foot was obtained. No further attempts were made to prepare chemically blown foams from PMDA-EtOH-DAB prepolymers.

Conclusions

Chemically blown foams of excellent quality can be prepared from BTDA-EtOH-DAB prepolymers. It was not found to be practical to prepare foams from the PMDA-EtOH-DAB prepolymers by using chemical blowing agents, probably because these prepolymers have no true melting point.

4.1D LIGHTWEIGHT FILLERS

Discussion

A commonly employed technique for obtaining cellular plastics consists of the incorporation of a lightweight, particulate filler, such as hollow bubbles, in a curable resin system. By curing such a mixture under the proper conditions, one can produce a molding which consists ideally of an ordered (or syntactic) three-dimensional array of unbroken, hollow bubbles in a relatively void-free plastic matrix.

The success of this approach depends on several important factors: (1) The resin or prepolymer must soften and flow sufficiently during the molding process to form a continuous, relatively void-free matrix. Insufficient resin flow would be expected to cause extensive breaking of even relatively strong bubbles. In this case, compaction of the mixture will result in extremely high stress levels due to point-to-point contact of bubbles and prepolymer particles. (2) Volatile byproducts of the curing reaction must be sufficiently low to preclude the possibility of

blistering or fracturing of the resulting molding during or following the curing process. (3) The bubbles used as a syntactic filler should be sufficiently strong to withstand the molding pressures.

Two commercially available, hollow fillers were considered as candidate materials for preparing syntactic Pyrrone foams: BJO-0930 Phenolic Microballoons* and B35D Glass Bubbles.**

Phenolic Microballoons

Type BJO-0930 Phenolic Microballoons is a free-flowing, reddish-brown powder consisting of microscopic hollow spheres of cured phenolic resin. The spheres have an average diameter of 0.0017 inch and are filled with an inert gas, primarily nitrogen, during manufacture. The true density of the stock product ranges from 14 to 16 pounds per cubic foot, as determined by fluid displacement using toluene as the displacement fluid. From past experience (reference 12), it was known that a fairly large fraction of these phenolic microballoons will fracture under even low molding pressures. Therefore, a select fraction of microballoons with a true density of 20 pounds per cubic foot produced by a pressure grading process at 700 psi was used in this program.

Pellet specimens were molded from a mixture of precipitated BTDA-EG-DAB prepolymer (tetraester type) and pressure-graded microballoons. Densities as molded were in the range of 53 to 73 pounds per cubic foot. The cell structure, examined microscopically, appeared to be excellent. However, a slow postcure in argon to a maximum temperature of 700° F resulted in severe degradation of the specimens. It was concluded that phenolic microballoons were not suitable as a lightweight filler since this material will apparently not withstand the temperature cycle required to postcure the Pyrrones.

*Union Carbide, Plastics Division
**3M, Reflective Products Division

Glass Bubbles

Type B35D Glass Bubbles is a free-flowing, white powder consisting of hollow glass spheres with a bulk density of approximately 13 pounds per cubic foot and a true density of 18-20 pounds per cubic foot. The particle size is comparable to that of the phenolic microballoons with 90 percent (by count) of the bubbles having a diameter between 0.0008 and 0.0032 inch. The type B35D Glass Bubbles are extremely resistant to external pressure with only 10 percent by volume failing (as reported by the manufacturer) when subjected to 2000 psi while immersed in water. The maximum safe use temperature for a prolonged period of time is reported to be approximately 1020° F.

Pellet specimens were molded from a mixture of 72 parts by weight precipitated BTDA-EG-DAB prepolymer (tetraester type) and 28 parts by weight of the B35D bubbles. Moldings of excellent quality with molded densities of 60.5 and 69.3 pounds per cubic foot were obtained. Postcuring in argon reduced these densities to 46.1 and 54.3 pounds per cubit foot, respectively. The quality of the postcured specimens was excellent.

It was concluded from the brief preliminary work just described that syntactic foams could be prepared from a mixture of Pyrrone prepolymer and the B35D Glass Bubbles. The development of processing conditions required to obtain high quality, syntactic foams is described in Section 6.2.

4.2 CONCLUSIONS

The following conclusions were drawn as a result of the feasibility studies.

- Oven Heating

  Oven heating can be used to prepare very fine-celled foams from ethylene glycol Pyrrone solutions synthesized from the diacid-diester of the dianhydride and DAB. By the proper control of synthesis conditions and oven temperature, BTDA-DAB foams with a density of 30 pounds per cubic foot and

PMDA-DAB foams with a density of 25 pounds per cubic foot can be made. However, the method is only feasible in preparing small sections of foam. Attempts to prepare larger sections of foam yield foams of higher densities (up to 45 pounds per cubic foot) which have a tendency to crack. It was concluded that the oven foaming method was not feasible for preparing relatively large foam sections and this method was not pursued further in this program.

- Volatile Fillers

  Foams of excellent quality were made by postcuring small moldings made from a mixture of precipitated Pyrrone prepolymer and powdered acrylic. The cell size distribution was narrow, with most cell diameters in the range of 0.002-0.004 inch. The foam density could be predictably controlled by adjustment of the relative proportions of prepolymer and acrylic. However, attempts to make larger foam sections by this method were unsuccessful due to incomplete volatilization of the acrylic during postcure. It was concluded that this method was not feasible for the preparation of large foam sections and no further effort was expended on this method.

- Chemical Blowing Agents

  Pyrrone foams of excellent quality were prepared by the controlled heating of mixtures of BTDA-EtOH-DAB Pyrrones and chemical blowing agents. Densities in the range of 15 to 45 pounds per cubic foot are attainable by this method. Nominal densities of 30 pounds per cubic foot were consistently achieved by molding a given charge weight to the correct volume. However, attempts to prepare a BTDA-EtOH-DAB foam with a density of 60 pounds per cubic foot were not successful. The quality of the chemically blown foam does not seem to be affected adversely when larger sections of foam are prepared. The chemically blown BTDA-EtOH-DAB foam

in the 30 pound grade appeared extremely promising and was chosen for further study and characterization. PMDA-EtOH-DAB prepolymers combined with chemical blowing agents did not yield cellular foams when heated. Further work on this system was discontinued.

- Lightweight Fillers

  Syntactic foams of good quality were prepared from mixtures of BTDA-EG-DAB prepolymer and glass bubbles. Densities in the range of 30 to 60 pounds per cubic foot are attainable by the use of lightweight fillers. Based on these preliminary results, little difficulty was anticipated in preparing syntactic foams with a nominal density of 60 pounds per cubic foot from this system. The 60-pound syntactic foam containing glass bubbles was chosen for further study and characterization.

  Syntactic foams containing phenolic microballoons were found to degrade severely during postcure. Further work on this system was discontinued.

5.0 CHEMICALLY BLOWN FOAMS

5.1 RESIN SYNTHESIS

General Procedure

The synthesis of the BTDA-EtOH-DAB Pyrrones consists of two main steps, the preparation of a BTDA-EtOH ester and reaction of this ester with an equivalent amount of DAB.

The BTDA is dissolved in excess absolute ethanol. After adding the required quantity of concentrated H_2SO_4, (which acts catalytically and shortens the time required to reach equilibrium) the mixture is maintained at reflux temperature for 24 hours or longer. After completion of the esterification, the excess ethanol is removed by distillation and the crude product is dissolved in ether or benzene. This solution is washed several times with aqueous sodium bicarbonate solution. The solution is then treated with a desiccant to remove any residual water and the solvent removed to give an ester of relatively low carboxyl content. An ester fraction of relatively high carboxyl content can be recovered by acidification and purification of the first bicarbonate wash fraction.

The low carboxyl ester (or a combination of low and high carboxyl ester) is then placed in a resin reaction kettle and heated under argon to the reaction temperature (Figure 5 shows the apparatus). An equivalent molar quantity of solid DAB is added to the ester while stirring. The resulting melt is stirred at the desired reaction temperature for a time usually somewhat in excess of that required for the evolution of ethanol to subside. The reaction is terminated by cooling the melt in an ice bath to obtain a hard glassy product. The addition of liquid nitrogen shatters the product into fine particles and allows convenient removal from the reaction vessel. Finally, the resin is ground to pass an 80-mesh sieve and dried under vacuum for 16 hours at 50°C.

Problems Related to Resin Synthesis

During the feasibility studies, batch-to-batch variations in the resins were found to affect markedly the foaming characteristics.

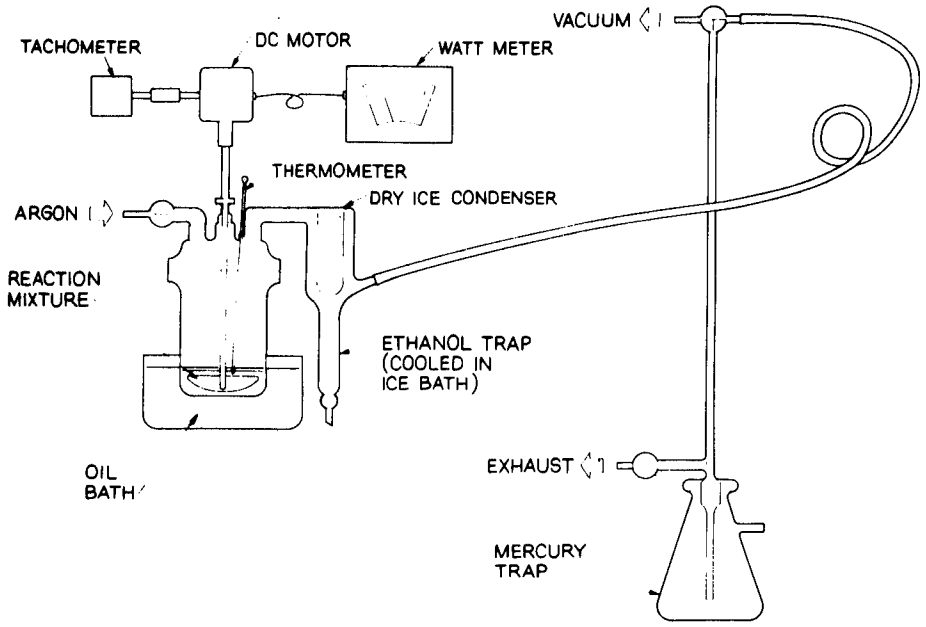


Figure 5. Apparatus for BTDA-EtOH-DAB Pyrrone Preparation

Foams of excellent quality were made early in the program after the development of satisfactory processing procedures. Toward the end of the feasibility studies, resins were synthesized which yielded foams of fair to poor quality.

At this point, attempts were made to define and measure those properties of the resins felt most likely to influence the foaming characteristics. These properties included the melting point, the inherent viscosity in DMF and the carboxyl content of the purified product obtained by the esterification of the BTDA with ethanol. Finally, an attempt was made to correlate these properties with the foaming characteristics. This approach met with only partial success. For example, it was found that resins prepared from BTDA esters of controlled carboxyl content and reacted to an inherent viscosity of 0.50 to 0.60 usually but not always yield chemically blown foams of good quality.

Since the BTDA-EtOH-DAB prepolymers are synthesized by a melt polymerization process, it is rather difficult to monitor the progress of the reaction by a viscosity measurement as in the case of the polymerizations conducted in ethylene glycol solution.

The degree of reaction may be followed by collecting and measuring the ethanol of reaction. However, in practice this was found to be impractical, since variable amounts of ethanol condensed and remained in the top of the reaction kettle and could not be measured. This was only partially eliminated by the intermittent application of partial vacuum.

One method which was partially successful involved measuring the power consumption of the stirring motor used to mix the contents of the reaction kettle. This method was also deemed unsatisfactory, since the power consumption was greatly affected by the degree to which the prepolymer adhered to the stirring paddle.

At present, the most reliable method seems to be to synthesize each batch at a time and temperature known by experience to yield a resin with good foaming characteristics. This method works well for

a given batch of ester. However, different batches of ester have been found to require different reaction times.

The carboxyl content of the ester was found to markedly influence the foaming characteristics of resins made from the ester. Early in the program, resins (Series 92 and 95) were prepared from esters of relatively high carboxyl content (8-10 equivalent-percent). Foams prepared from these resins in most cases ranged in quality from fair to excellent. Toward the end of the feasibility studies, resins (Series 97) were prepared from an ester of much lower carboxyl content (1.5 equivalent-percent). Ten batches of resin were prepared from this ester batch under a wide variety of conditions. Only one of these resins, No. 97F with an inherent viscosity of 0.52 yielded a good foam. Most of the remaining resins gave non-uniform foams of poor quality. It was noted that the low carboxyl ester reacted much more slowly with the DAB than the high carboxyl esters to give resins of comparable inherent viscosity. The principal results are listed in Table VII.

The foregoing results indicate strongly that esters of high carboxyl content yield resins with better foaming characteristics than esters of low carboxyl content. However, the preparation of esters of relatively high (and controlled) carboxyl content is not simple. The preparation of high carboxyl esters probably is a result of inadequate bicarbonate extraction and washing procedures. The alternative procedure adopted consists of the blending of two ester fractions, that is the low carboxyl ester obtained as the main product of the esterification and the relatively high carboxyl fraction obtained by acidification of the first bicarbonate wash fraction.

A series of resins was prepared by reacting DAB with mixed esters with carboxyl contents ranging from 3.9 to 8.4 equivalent-percent. As previously noted, reaction times were considerably shorter for resins made from high carboxyl resins. Surprisingly, resins prepared from esters with a high carboxyl content did not yield consistently good foams. However, a mixed ester with a carboxyl content of 3.9 equivalent-percent was used in preparing a resin with excellent foaming

Table VII. Effect of Synthesis Conditions on Foaming Characteristics of BTDA-EtOH-DAB Prepolymers

Resin Number	Carboxyl Content of Ester Eq-%	Reaction Time, Minutes	Reaction Temperature, °C	Inherent Viscosity (Note 1)	Quality of Foam	Remarks
92A	9.6	34	165	-	Excellent	Uniform
92B		23	180	-	Fair	Coarse Cells
92C		19	175	-	Fair	Slightly Non-Uniform
92D		20	180	0.60	Good	Slightly Non-Uniform
95A	7.8	45	180	0.53 (Note 2)	Good	Slightly Non-Uniform
95B		40	180		Excellent	Uniform Cells
95C		45	180		Excellent	Uniform Cells
95D		35	180		Poor	Non-Uniform; Fractured
95E		30	180	-	Good	Nearly Uniform
95F		32	180	-	Good	Uniform, Except one large cell
97A	1.5	100	180	0.46	Poor	Low Density; Non-Uniform
97B		75	180	0.38	Poor	Non-Uniform; Large Cells
97C		85	180	-	Poor	Non-Uniform; Large Cells
97D		115	180	0.49	Poor	Non-Uniform; Large Cells
97E		80	180	-	Poor	Non-Uniform; Large Cells
97F		170	180	0.52	Good	Few Large Cells
97G		185	180	0.57	Poor	Non-Uniform
97H		125	180	0.46	Fair	Non-Uniform
97J		110	200	0.64	Very Poor	Very Coarse Cells
97K		95	200	0.74	Extremely Poor	Large Fractures

Note 1: Determined at concentration of 2.5 gm/100cc in dimethylformamide
Note 2: Inherent viscosity run on blended batches

characteristics. Subsequently, a large number of resin batches was prepared from mixed esters with a carboxyl content of 3.5 equivalent-percent. With few exceptions, the chemically blown foams prepared from these resins were uniform in cell structure.

Standard Synthesis Procedure

Based on the difficulties described in the preceding section, standard synthesis procedures for the preparation of the ester and the resin were adopted for the remainder of the program. The following preparations are typical:

E1706-4 Preparation of BTDA-Ethanol Ester

BTDA, 4508 gm (14.0 mole), was slurried in 9 liters of anhydrous ethanol, and the mixture heated to reflux. After the BTDA had dissolved, 700 ml of concentrated sulfuric acid was added dropwise with constant stirring. The mixture was stirred at reflux for 30 hours. Excess ethanol (approximately 7 liters) was then distilled off until the volume of reactants was reduced to approximately one third of the original. The crude product was taken up in 7 liters of ether and washed twice with water. It was then washed three times with equal volumes of saturated aqueous sodium bicarbonate solution until acidification of the bicarbonate washes failed to precipitate carboxyl salts. The partially esterified product from the first bicarbonate wash was recovered by acidification and taken up in ether.

Both fractions of ester were dried as ether solutions with anhydrous magnesium sulfate. Residual solvents in both fractions were then removed under vacuum on a rotary still at 150°C for 3 hours. The low carboxyl ester had a carboxyl content of 0.9 equivalent percent and weighed 3457 gm (53 percent of theoretical). The high carboxyl ester contained 22.1 equivalent percent carboxyl and weighed 1487 gm.

E1706-8 Preparation of BTDA-EtOH-DAB Resins from E1706-4 Esters

Eleven batches of BTDA-EtOH-DAB resin were prepared from the E1706-4 mixed esters. A mixture of 123.6 gm of low carboxyl ester and 16.4 gm of high carboxyl ester (total of 0.3 mole) was heated to 180°C under argon and solid DAB, 64.3 gm (0.3 mole), was added while

stirring. The reaction mixture was stirred for 100 minutes at 180°C. The resin kettle was evacuated briefly every 30 minutes to facilitate removal of ethanol of reaction. The reaction was terminated by cooling the melt in an ice bath. The glassy product was shattered into fine particles by the addition of liquid nitrogen. Finally, the resin was ground to pass 80 mesh and dried under vacuum for 16 hours at 50°C.

The inherent viscosity of each of the resins was determined at a concentration of 2.5 gm/100 cc of dimethylformamide. The results indicate a fair degree of reproducibility. The average inherent viscosity was 0.53 with a standard deviation of 0.02.

E1706-24 Preparation of High Purity BTDA-Ethanol Tetraester

BTDA (1612.1 gm, 5.0 mole) was slurried in 3100 ml absolute ethanol. Concentrated sulfuric acid (250 ml) was added dropwise to the mixture, and the pot was heated to gentle reflux. The BTDA dissolved, and the reaction was stirred at gentle reflux for 40 hours.

The excess ethanol was removed from the pot by distillation (about 1500 ml ethanol were distilled out), and the crude product was taken up in 5000 ml benzene. This benzene solution was shaken several times with fresh double-distilled water. Partially reacted ester was removed from the product by shaking the benzene solution several times with fresh 10 percent aqueous sodium bicarbonate solution (USP bicarbonate in double-distilled water was used), and the first bicarbonate wash was set aside for subsequent recovery of the partially reacted ester. The remaining tetraester solution was then dried by shaking several times over fresh anhydrous magnesium sulfate, and filtering out the solids. The benzene was then evaporated from the tetraester by distillation at ambient pressure, and solvent residues were removed under vacuum by heating the ester on a rotary still for 3 hours at about 5 mm mercury and 150°C bath temperature. The low carboxyl fraction weighed 1009.1 gm (43 percent of theoretical yield), it had an equivalent percent carboxyl content of 1.5, and an equivalent weight of 132.6 by analysis. The high carboxyl fraction weighed 571.1 gm; it had an equivalent percent carboxyl content of 24.4, and an equivalent weight of 116.6 by analysis.

This batch of high purity BTDA-ethanol-DAB ester was used to prepare the following resin batches.

E1706-25-1: Ten Percent Carboxyl (By Equivalence)

A mixture of BTDA-ethanol ester E1706-15 containing 90.5 gm of low carboxyl ester and 47.3 gm high carboxyl ester (137.8 gm, 0.3 mole mixed), was heated under argon to 180°C with constant stirring. Solid DAB (64.3 gm, 0.3 mole) was added under argon to the stirred ester, and the mixture was reacted 5 minutes at a temperature of about 140-145°C. The system was then evacuated to remove ethanol of reaction, and after a total of 10 minutes stirring at 140-145°C; the pot was cooled rapidly in an ice bath, liquid nitrogen poured over the melt to shatter it, and the resulting product stored under argon. After being ground to a fine powder, the glass was dried overnight at 50°C under vacuum.

E1706-25-2: Twenty Percent Carboxyl (By Equivalence)

A mixture of BTDA-ethanol ester E1706-15 containing 38.8 gm of low carboxyl ester and 95.6 gm of high carboxyl ester (134.4 gm, 0.3 mole mixed), was heated under argon to 180°C with constant stirring. Solid DAB (64.3 gm, 0.3 mole) was added under argon to the stirred ester, and the mixture was stirred several minutes at about 140°C. The system was evacuated to remove ethanol of reaction. After a total of about 4 minutes reaction at about 145°C, the melt could no longer be stirred. The pot was cooled rapidly in an ice bath, and liquid nitrogen poured over the melt to shatter it. The resulting product was ground to a fine powder, dried in a vacuum oven overnight at 50°C, and stored under argon.

E1706-28-1: Preparation of BTDA-Ethanol-DAB Pyrrone from High Purity Ester E1706-24

A mixture of low and high carboxyl esters having a 3.5 equivalent percent carboxyl content, and containing 128.2 gm of low carboxyl ester and 11.8 gm of high carboxyl ester (140.0 gm, 0.3 mole mixed

ester), was heated under argon to 180°C; and solid DAB (64.3 gm, 0.3 mole) was added under argon, to the stirred ester. The resulting melt was reacted at 180°C for 100 minutes under argon (the system was evacuated every 30 minutes to remove ethanol of reaction). The melt was then cooled rapidly in an ice bath, and liquid nitrogen poured over it to shatter the Pyrrone glass. It was ground to a fine powder, dried overnight in a vacuum oven at 50°C, and stored under argon.

E1706-36: Preparation of BTDA-Ethanol-DAB Pyrrone from Combined Ester

A 3.5 equivalent percent free carboxyl ester was prepared by mixing 339.6 gm of BTDA-EtOH low carboxyl ester E1706-15 with 45.3 gm of BTDA-EtOH high carboxyl ester E1706-24.

This mixed ester was heated under argon to 180°C in a 15 gallon high temperature circulating bath and 176.8 gm (0.83 mole) of solid DAB was added. The entire reaction system was evacuated every 30 minutes, after the DAB addition, to rapidly remove the evolved ethanol. The mixture was stirred at 180°C for 105 minutes and the resulting melt was then rapidly cooled in an ice bath. After cooling, the solid product was shattered into small fragments by pouring liquid nitrogen over it.

E1706-34: Preparation of BTDA-Ethanol Combined Ester

A 2298 gm (5 mole) mixture of residual fractions of BTDA-EtOH ester (approximately 75 percent esterified) from prior ester runs was dissolved in one gallon of anhydrous ethanol, and 100 ml of concentrated sulfuric acid were added dropwise to the mixture. This reaction mixture was run at reflux for 40 hours, with the excess ethanol continuously removed by distillation. The crude product was taken up in one gallon of benzene and the benzene phase was shaken up alternately in fresh water, in 10 percent aqueous sodium bicarbonate solution and again in fresh water. The benzene phase was then dried over anhydrous magnesium sulfate and the product recovered by distilling off the benzene.

Residual solvents were then removed by vacuum distillation in a rotary still for three hours at a bath temperature of 150°C. The resultant product weighed 1348 gm (57 percent of the theoretical yield based on a 75 percent esterified starting material).

This product was combined with the remaining BTDA-EtOH low carboxyl ester fractions from prior esterification reactions, to make a stock combined ester weighing 3570 gm. This stock ester was designated E1706-34 combined ester. This ester was analyzed and found to have an equivalent weight of 122.2 and an equivalent unreacted carboxyl content of 0.11 percent.

The remaining partially esterified BTDA-EtOH ester fraction was recovered from the first aqueous bicarbonate wash by acidification with hydrochloric acid. The aqueous phase from this recovery was decanted and this new high carboxyl content fraction was taken up in 2 liters of benzene. The benzene phase was shaken with fresh water and dried over anhydrous magnesium sulfate. After drying was completed, the benzene was distilled off and this new high carboxyl content ester fraction was taken up in one liter of ethanol. This combined ester was used to prepare a 10 pound batch of BTDA-Ethanol-DAB resin in the following manner.

E1706-36: Preparation of Master Batch of BTDA-Ethanol-DAB

A total of nine 520 gram batches of the Pyrrone resin were prepared in the following manner.

A 334.3 gm quantity of E1706-34 low carboxyl ester was blended with 52.8 gm of E1706-24 high carboxyl ester to make up 387.1 gm (0.83 mole) of combined ester with an equivalent free carboxyl content of 3.5 percent.

Each 0.83 mole batch of this combined ester was heated to 180°C under argon and 176.8 gm (0.83 mole) of solid DAB was added. The reaction system was evacuated after addition of the DAB, and every half hour thereafter, to remove the ethanol of reaction. Each batch was run for 110 minutes at 180°C, then cooled rapidly in an ice bath.

Liquid nitrogen was then poured over the resin melt to shatter it into small particles. The nine batches were blended and weighed. The total weight of the blended batches was 4635.2 gm. This product was stored under argon for future use in producing chemically blown foams.

E1706-41: Preparation of BTDA-Ethanol-DAB Master Batch

Seven nominal two pound batches of BTDA-ETOH-DAB resin were prepared in the following manner.

The ester was prepared by heating a 4508.4 gm (14.0 mole) quantity of BTDA slurried in 8.5 liters of anhydrous ethanol to gentle reflux. A 700 ml quantity of concentrated sulfuric acid was added dropwise, and the mixture was refluxed for 40 hours with approximately one gallon of ethanol removed from the reaction mixture.

One gallon of benzene was added and the mixture heated again to reflux and reacted for an additional 12 hours using an azeotropic trap to remove the water of reaction. The product was then shaken several times with fresh water and neutralized by shaking with saturated aqueous sodium bicarbonate solution. The first bicarbonate wash was set aside for later recovery of the partially esterified product.

The resultant benzene solution was dried over anhydrous magnesium sulfate after shaking with fresh water. The solution was filtered and the benzene evaporated from the ester by distillation. Residual solvents were removed by vacuum distillation of the ester at a bath temperature of 150°C.

The tetraester fraction weighed 5324.9 gm (81 percent of the theoretical yield); it had an equivalent percent free carboxyl content of 0.44 and an equivalent weight of 113.2.

The partially reacted ester was recovered from the bicarbonate wash by neutralization with hydrochloric acid. It was then taken up in benzene, washed with fresh water, dried over anhydrous magnesium sulfate and the benzene evaporated by distillation. Residual solvents were again removed by vacuum distillation at a bath temperature of 150°C. This fraction had an equivalent percent carboxyl content of 23.8.

A mixed ester with a 3.5 equivalent percent carboxyl content was prepared by blending 5324.9 gm of the low carboxyl fraction ester with 779.7 gm of the high carboxyl fraction ester.

The BTDA-EtOH-DAB resin E1706-41 was prepared as seven nominal two pound batches in the following manner. A 774.0 gm (6.64 equivalent) of mixed ester was heated to 180°C under argon and 353.6 gm (6.64 equivalent) of solid DAB was added. The reaction mixtures were stirred under argon for 130 minutes each. After the initial addition of the DAB, the system was evacuated to remove ethanol of reaction, and this procedure was repeated every half hour thereafter for each batch prepared. The resin was cooled rapidly in an ice bath and liquid nitrogen poured over the resin melt to shatter it into small particles. The seven batches were blended as master batch E1706-41 and stored under argon for future use in molding chemically blown foams.

The various batches of BTDA-Ethanol-DAB Pyrrone resins were used in various stages of the foam development program described in Section 5.2.

5.2 FOAM DEVELOPMENT

Study of Processing Variables

Prior to the preparation of large sections of chemically blown foam, several processing variables were studied further.

A block of chemically blown foam measuring nominally 1 x 4 1/2 x 6 inches was prepared from a master batch made by blending the eleven batches of E1706-8 resin. A charge weight of 275 gm of resin containing 0.5 percent of Celogen OT blowing agent was taken to make a molding with a nominal density of 30 pounds per cubic foot. However, considerable flow from the mold occurred during cure resulting in a block with a density of only 17.1 pounds per cubic foot. The process was the same as used previously: the charge was placed in the mold and preformed, the punch released and a shim inserted, the mold was

placed in a cold oven, and the temperature increased to 275°F, held at 275°F for 5 hours and increased to 500°F over a period of 5 hours.

Excessive flow also occurred in molding several 2-1/4-inch diameter discs with densities ranging from 24.6 to 28.5 pounds per cubic foot. At this point, three 2-1/4-inch diameter discs were prepared from a prepolymer containing, respectively, 0.10, 0.25 and 0.50 percent Celogen OT as a blowing agent. All of the foams were fine-celled and uniform. The foam containing only 0.10 percent blowing agent showed no tendency to flow from the mold during cure and a molding with a nominal density of 30 pounds per cubic foot was obtained. In preparing the remainder of the 30 pound per cubic foot chemically blown foam moldings, it was decided to lower the blowing agent concentration from 0.50 to 0.10 percent to allow better control of the density.

An additional series of resins was made from mixed esters in which the carboxyl content varied from 2.0 to 8.0 equivalent percent. The results confirmed those obtained previously; that is, resins with the best foaming characteristics are made from esters with the carboxyl content in the range of 3 to 4 equivalent percent.

An effort was made to prepare foams with finer cells by the addition of a liquid surfactant, Union Carbide's L-520. The use of this surfactant did not result in any improvement. In fact, the foam containing the surfactant was much coarser and more irregular in cell structure than a control foam without the surfactant.

Further evidence was obtained which indicates that the degree of purification of the BTDA-EtOH ester from which the resins are prepared is probably the most important single factor in preparing uniform, fine-celled foams. One BTDA-EtOH ester, E1706-12 was prepared by refluxing BTDA and ethanol in the presence of sulfuric acid for 60 hours. Purification consisted of distilling off most of the excess ethanol, removing any water of reaction by azeotropic distillation with benzene, washing with water and sodium bicarbonate solution and drying over anhydrous magnesium sulfate solution. The benzene was removed by distillation and by evaporation in a rotary

still to give a product with a carboxyl content of 0.7 equivalent percent. A test batch of resin, E1706-14-1, was made by reacting DAB with a portion of this ester to which had been added sufficient high carboxyl content ester to give an overall carboxyl content of 3.5 equivalent percent. A foam prepared from this resin was extremely poor in quality, with many cells larger than 1/8 inch in diameter.

The remaining E1706-12 ester was then dissolved in benzene, washed twice with water, dried over anhydrous magnesium sulfate and separated from the benzene in a rotary still. Another batch of resin, E1706-14-2, was prepared from this reworked ester. A foam prepared from this resin was of good quality and had a uniform cell structure. It is apparent from these results that the purification of the BTDA-EtOH ester is extremely critical in preparing foams from the resin made from the ester.

Preparation of Samples

Chemically blown foam samples with nominal densities of 20 and 30 pounds per cubic foot were prepared and submitted to NASA for characterization. The complete set of samples consisted of 30 1-inch long cylindrical specimens, 20 with a diameter of 2 inches and 10 with a diameter of 1 inch.

The 2-inch specimens were made as follows: A charge weight of 34.40 gm of powdered BTDA-EtOH-DAB resin containing 0.1 percent Celogen OT was placed in a 2 1/4-inch diameter mold and preformed at 5000 psi. The punch was raised, a shim was inserted to give an inside axial mold dimension of 1.125 inches, and the entire assembly was secured with a C-clamp. The mold assembly was placed in a cold oven and the temperature was increased to 275°F in about 20 minutes. The temperature was maintained at 275°F for 5 hours and programmed from 275° to 500°F over a period of 5 hours. After cooling to room temperature, the moldings were removed from the mold, weighed and measured. The entire set of specimens was postcured in argon from 300° to 700°F over a period of 5 days. Following postcure, each of the specimens was again weighed and measured.

The procedure was the same for the one-inch diameter specimens, except that a charge weight of 8.57 gm was placed in a 1-1/8-inch diameter mold.

The density of each of the specimens before and after postcure was calculated from the appropriate weight and dimensions. The weights, dimensions and calculated densities lie within a fairly narrow range (see Table VIII), indicating that a reproducible material and process have been achieved. The combined molding and postcuring shrinkage was somewhat higher than had been anticipated, with the result that each of the specimens was slightly smaller in both dimensions than desired.

Two billets were molded from a blended batch of BTDA-EtOH-DAB resins in the 6-1/2 x 9 inch mold. The finely powdered resin-blowing agent mixture (751 gm) was distributed evenly in the mold and subjected to 1000 psi pressure for a few seconds to give a uniform preform. The punch was then raised and shimmed to give a distance between the top and bottom punches of 1.55 inches. After clamping, the mold was placed in a cold oven. The temperature was then increased to 275°F in about 10 minutes, held at 275°F for 5 hours,

Table VIII. Weight, Dimensions, and Densities of Chemically Blown BTDA-EtOH-DAB Foam Specimens

Property	Nominal 1 inch diameter		Nominal 2 inch diameter	
	As molded	Post-cured	As molded	Post-cured
Average Weight, gm Standard Deviation	7.27 0.10	5.87 0.07	29.74 0.44	23.69 0.34
Average Length, inches Standard Deviation	1.042 0.010	0.978 0.012	1.050 0.012	0.980 0.012
Average Diameter, inches Standard Deviation	1.052 0.0031	0.987 0.0023	2.108 0.0044	1.969 0.0033
Average Density, lb/cu ft Standard Deviation	30.58 0.45	29.89 0.40	30.89 0.32	30.18 0.36

increased from 275° to 500°F over a period of 5 hours, and cooled to room temperature. Finally, the billets were postcured in argon from 275° to 700°F over a period of 5 days. Table IX lists the dimensions and density of each billet as molded after postcure.

Table IX. Dimensions and Densities of Chemically Blown BTDA-EtOH-DAB Foam Billets

Property	Billet 1		Billet 2	
	As molded	Post-cured	As molded	Post-cured
Weight, gm	661	525	664	525
Dimensions, inches	1.549 x 6.250 x 8.625	1.450 x 5.840 x 8.082	1.531 x 6.240 x 8.637	1.436 x 5.833 x 8.082
Density, lb/cu ft	30.1	29.2	30.6	29.5

After the processing parameters for the molding of 30 pound per cubic foot chemically blown foams had been established, an attempt was made to extend the density range of the chemically blown foams.

Chemically blown foams were prepared from the following prepolymers:

E1706-25-1, 10 equivalent-percent carboxyl content
E1706-25-2, 20 equivalent-percent carboxyl content
E1706-25-3, 15 equivalent-percent carboxyl content

Foams of three nominal density grades were prepared from E1706-25-1: 30, 45, and 60 pounds per cubic foot. The 30 pound foam was of fair quality with mostly fine cells and a few large cells. The 45 pound foam was extremely fine celled and uniform but showed some evidence of fine cracking at and near the edges. The 60 pound foam was also very fine celled but split into several large pieces during cure. The results seem to indicate no particular advantage in the use of this prepolymer in place of the standard prepolymer prepared from the ester with 3.5 equivalent-percent carboxyl content.

Chemically blown foams could not be prepared from either E1706-25-2 (20 equivalent-percent carboxyl) or E1706-25-3 (15 equivalent-percent carboxyl). In each case, the preformed mixture of prepolymer and blowing agent failed to foam in the mold during the heating cycle. Instead, the mixtures cured to hard, somewhat porous discs with densities in the range of 60-65 pounds per cubic foot.

Effect of Oven Advancement on Properties

Small quantities of BTDA-ethanol-DAB, E1706-28-1 were heated in a vacuum oven for various times at 275° and 350°F and the result of this high temperature exposure on the melting point was determined. At both temperatures, the melting point decreased after short heating times and then increased with longer heating periods. The following table summarizes the results.

Time at 275°F, Minutes	Melting Point, °C	Time at 350°F, Minutes	Melting Point °C
0	120-125	0	120-125
15	120-125	15	100-105
30	115-120	30	105-110
45	110-115	45	115-120
60	105-110	60	115-120
75	97-100	75	120-125
90	95-100	90	120-125
210	110-115	105	120-125
		120	125-130

Larger quantities of No. 1706-28-1 were heated under vacuum 90 minutes at 275°F, 210 minutes at 275°F, and 120 minutes at 350°F, respectively. After advancement, the prepolymers were reground, compounded with 0.1 percent Celogen OT and cured into foams with a nominal density of 30 pounds per cubic foot. A distinct improvement in fineness of cell structure and uniformity was noted in those foams made from the prepolymer heated at 275°F. The foam prepared from the prepolymer heated at 350°F was only of fair quality.

Chemically blown foams of greatly improved quality were prepared from prepolymers which had been advanced by controlled heating in a vacuum oven. The effect of various heating periods up to 16 hours at 275°F on the foaming characteristics was studied. Excellent foams with densities of 30 and 42 pounds per cubic foot with fine, uniform cell structures were obtained from prepolymer E1706-28-1 heated for 3-1/2 hours at 275°F. Preliminary attempts to prepare a good 60 pound foam were unsuccessful. The cell structure was uniform, but the specimen contained several large fracture planes.

A series of three preliminary low density chemically blown foams was molded with BTDA-EtOH-DAB resin E1706-28 and Celogen AZ. The foams were molded in an attempt to determine whether chemically blown foams with relatively uniform cell structure and structural integrity could be formed in the 5-15 pound density range.

These three foams, designated Y-1, Y-2 and Y-3 were molded in a one inch diameter mold with vacuum oven advanced E1706-28 resin and blowing agent contents of 0.1 percent, 0.2 percent and 0.3 percent. The cured densities of these foams were 14.3, 13.6 and 13.7 pounds per cubic foot respectively. No attempt was made to post-cure these foams, since they were considered to be preliminary attempts to understand the behavior of the resin under low density foaming procedures.

All three foams appeared to possess a fair degree of toughness, an equal distribution of nonuniform sized cells and no evidence of foam fractures due to curing temperatures or cooling.

A series of five chemically blown foams was molded in an effort to establish the processing conditions necessary for the formation of a resin formulation, which will enable a wide density range of foams to be molded.

The first foam was molded with BTDA-EtOH-DAB resin E1706-36 which had been advanced to 425°F in a vacuum oven and held at 425°F for 7 minutes. This material was ground and blended with 0.3 percent Celogen AZ and molded in a 1-1/8 inch mold from 300° to 600°F. This foam was designated Y-4, sectioned and found to possess an even distribution of uniform cells. The density of this foam was calculated to be 14.9 pounds per cubic foot. This foam was not postcured.

The second foam was molded with E1706-36 resin which had been advanced to 338°F in a vacuum oven and held at 338°F for one hour. The advanced resin was ground and molded in a 1-1/8 inch mold from 300° to 600°F without the addition of any blowing agent. This foam was designated Y-5, sectioned and found to possess an uneven distribution of relatively large cells. The density of this foam was calculated to be 15.1 pounds per cubic foot. This foam was not postcured.

A series of three foams was molded from E1706-36 resin advanced in the same manner as that used for foam Y-5. This advanced resin was ground and blended with 0.1 percent Celogen OT. Charge weights were calculated to give foams with final densities of 15, 30 and 45 pounds per cubic foot. The proper amounts of resin were charged into 1-1/8 inch molds at room temperature and pressure was applied to compact the resin in the molds. The molds were then spaced to predetermined volumes and the mold rams clamped into place. These molds were then placed in an oven and heated from room temperature to 275°F, held at 275°F for five hours, then heated from 275° to 500°F in five hours and cooled to room temperature. These three foams were designated Y-6, Y-7 and Y-8, and the densities were calculated to be 15.3, 30.5 and 42.9 pounds per cubic foot, respectively. The foams were sectioned and it was found that all but the 15 pound foam had evenly distributed uniform cells. The 15 pound foam had an uneven distribution

of large cells very much like foam Y-5. None of these foams were postcured. The physical properties and processing conditions of these five foams are summarized in Table X.

A small quantity of BTDA-EtOH-DAB resin E1706-36 was heated for 3 hours at 300°F, ground and a portion blended with 0.1 percent Celogen OT blowing agent. An equivalent amount of this material was set aside and not blended with the blowing agents. A set of six foams was molded with these materials; three foams with nominal densities of 15, 30 and 45 pounds per cubic foot were molded with the resin containing the blowing agent and a similar set of three with resin not containing the blowing agent. The results of these moldings are summarized in Table XI.

Table X. Processing Parameters and Densities of Chemically Blown Foams

Foam	Percent Blowing Agent	Mold Size	Charge Weight (gms)	Density (lb/cu ft)	Description of Foam
Y-4	0.3	1-1/8 inch (diameter) x 1 inch	4.00	14.9	Evenly distributed uniform cells – no cracks
Y-5	-	1-1/8 inch (diameter) x 1 inch	4.00	15.1	Non-uniform cells – no cracks
Y-6	0.1	1-1/8 inch (diameter) x 1-1/8 inch	4.50	15.3	Non-uniform cells – no cracks
Y-7	0.1	1-1/8 inch (diameter) x 1-1/8 inch	8.60	30.5	Evenly distributed uniform cells – no cracks
Y-8	0.1	1-1/8 inch (diameter) x 1-1/8 inch	12.90	42.9	Evenly distributed uniform cells – no cracks

Based upon investigation of the foaming parameters it appears that optimum chemically blown foams with densities of 15, 30 and 45 pounds per cubic foot will be formed with BTDA-EtOH-DAB resins advanced in the 300° - 350°F range. A small amount of blowing agent appears to aid in obtaining a uniform cell structure.

The processing conditions necessary to produce acceptable 45 pound chemically blown foams were investigated. Both Celogen RA

Table XI. Properties of Chemically Blown Foams

Nominal Density (lb/cu ft)	Blowing Agent (percent)	Molded Density (lb/cu ft)	Appearance
15	0.1	14.9	Non-uniform cell structure
15	-	15.4	Non-uniform cell structure
30	0.1	30.5	Good cell structure, no cracks
30	-	30.3	Good cell structure, no cracks
45	0.1	42.6	Good cell structure, broke in mold
45	-	42.0	Good cell structure, broke in mold

(blowing temperature approximately 425°F) and Celogen AZ (blowing temperature approximately 350°F) were used as blowing agents and the advancing conditions were varied between 3 hours at 300°F in a vacuum oven to 6-1/2 hours at 275°F in a vacuum oven. Molding in both a press and an oven were investigated. The material was introduced to each of these both cold and at temperature.

Initial results of this investigation indicate that the most uniform foams with acceptable cell structure were produced using resin which had been advanced 6-1/2 hours at 275°F in a vacuum oven. This resin blended with 0.1 percent Celogen AZ, introduced to a hot mold and cured in a forced draft oven appeared to produce the best 45 pound foam.

Several 4-1/2 inch x 6-1/2 inch billets of chemically blown foam with a nominal density of 15 pounds per cubic foot were attempted, however the blown material did not appear to fill the mold. Thus, the charge weights of the larger billets were increased on successive billets until billets

with no appreciable surface depressions were obtained. The increased charge weight necessary to fill the mold volume increased the density of the molded foams to nominally 20 pounds per cubic foot.

Several chemically blown foams with a nominal density of 45 pounds per cubic foot were molded by introducing the charge into the mold heated to 175°F and 250°F. The lower temperature appeared to give a foam with a uniform cell structure and no signs of case handening.

The foam development program indicated that chemically blown foams of small cross-section could be successfully molded in the 15 to 40 pound per cubic foot density range but when attempts were made to scale up to larger billets, the foam behavior was erratic. This would seem to indicate that the lower density foams are very critical with respect to the flow characteristics and heat exchange through the cellular resin matrix.

The higher density foams in the greater number of cases possessed uniform structure with fine evenly distributed cells, however, they have a tendency to undergo catastrophic shrinkage cracking. Further investigation will be necessary to eliminate this cracking. Those molded foams with densities between 15 and 40 pounds per cubic foot which were of relatively uniform cell structure with minimal cracking were used to supply the material for the 1 inch diameter and 2 inch diameter cylinders and large billets required for evaluation by NASA-LRC. The characterization of the available foam specimens is summarized in the following sections.

5.3 FOAM CHARACTERIZATION

The characterization of the chemically blown foams involved a continuous evaluation as the development progressed and a final evaluation of the physical properties of the optimized chemically blown foams.

The continuous evaluation of the chemically blown foams consisted of visual observation of the sectioned foams and calculation of the "as molded" and postcured densities of these foams. These observations are discussed throughout Sections 4.0 and 5.2 where applicable to the

foam development study. In addition to these properties, the shrinkage, isothermal weight loss, compressive strength and thermal conductivity were checked at various stages of the feasibility study and development program.

Once it was felt that the 30 pound per cubic foot BTDA-EtOH-DAB chemically blown foam system had been optimized, a series of billets was molded according to the conditions developed, and test specimens cut and submitted for physical testing. Specimens of the nominal 20 and 40 pound per cubic foot foams were characterized where available.

Volume Fraction of Continuous Voids

Impregnation with an epoxy resin under moderate pressure was used to estimate the fraction of continuous voids in small pieces cut from 6-1/2 x 9 inch billets of chemically blown foam with nominal densities of 20, 30 and 40 pounds per cubic foot. The method consists of vacuum-pressure impregnation of preweighed, 1-inch cubes of the foam with a mixture of 100 parts by weight of Epon 828* epoxy resin and 37 parts by weight of ZZL 0803** hardener. The specimens were covered with the resin-hardener mixture while under vacuum and subjected to a pressure of 50 psig for 1 hour. After wiping the excess resin from the impregnated foam blocks with acetone-moistened tissues, the blocks were reweighed. The volume fraction pregnable voids (assumed to be the same as the volume fraction of continuous voids) was calculated from the unimpregnated foam density, the weight increase as a result of impregnation and the density of the uncured impregnating resin.

The volume fraction of continuous voids was found to be 0.82, 0.66 and 0.38 respectively for nominal 20, 30 and 40 pound per cubic foot chemically blown foams.

---

*Shell Chemical Company, Plastics and Resins Division
**Union Carbide Chemicals Company

Specific Heat

The specific heat of 30 pound per cubic foot chemically blown BTDA-EtOH-DAB foam was determined by the method of mixtures. Precautions were taken to ensure complete immersion and thorough mixing of the foam in the water contained in the calorimeter to ensure virtual thermal equilibrium.

Two runs were made with 30 pound per cubic foot chemically blown foam which had been postcured to 700°F. In one case the foam was finely powdered and in the other diced into small cubes roughly 3/8 inch on the side. The results were fairly consistent, with a value of 0.276 calories/gram/°C obtained for the powdered Pyrrone and 0.262 calories/gram/°C for the diced material.

The nominal 20 foot per cubic foot density chemically blown foam had a specific heat of 0.254 calories/gram/°C when determined on the diced material. This value is close to previous values thus indicating that the specific heat can be expected to be 0.25-0.28 calories/gram/°C when determined between 8° and 100°C.

Thermal Conductivity

The thermal conductivity of two 3 x 3 x 1/8 inch slabs of nominal 30 pound per cubic foot chemically blown foam was determined by the Cenco-Fitch method. This method is a dynamic test in which the test specimen is placed between a heat source and a heat sink. The thermal conductivity is then determined from the rate of temperature rise of the heat sink.

The individual thermal conductivities of the two slabs of foam were determined to be 0.60 and 0.73 BTU/inch/hour/foot^2/°F which gave an average value of 0.66 BTU/inch/hour/foot^2/°F (2.3×10^{-4} calories/cm/sec/cm^2/°C).

Compressive Strength and Modulus

The compressive strengths and moduli of nominal 20 and 30 pound per cubic foot chemically blown foams were determined at -100°F, room temperature, and 700°F according to ASTM Method D695. Five 1/2 inch diameter by one inch long specimens of the 30 pound per cubic foot material were tested at each of the temperatures in the foaming direction and perpendicular to the foaming direction. Most of the specimens exhibited shattering fractures due to the relatively brittle nature of the material and the load-deflection curves were fairly linear to the break point. Thus, no reliable yield points could be determined and the compressive strengths reported are "ultimate" values. The compressive strength values obtained for these foams are recorded in Table XII.

Table XII. Compressive Strength and Modulus of 30 Pound Per Cubic Foot Chemically Blown Foam

Test Temperature °F	Average Compressive Strength, psi		Average Modulus, psi	
	Loaded in Foaming Direction	Loaded Perpendicular to Foaming Direction	Loaded in Foaming Direction	Loaded Perpendicular to Foaming Direction
-100	1720	2000	0.9×10^5	1.0×10^5
Room Temperature	1480	3120	1.0×10^5	1.3×10^5
700	1490	1450	2.5×10^4	6.2×10^4

Specimens of the nominal 20 pound per cubic foot chemically blown foam were tested in the foaming direction only at the same temperatures. The results of these tests are given in Table XIII.

Table XIII. Compressive Strength and Modulus of 20 Pound Per Cubic Foot Chemically Blown Foam

Test Temperature °F	Average Compressive Strength, psi	Average Modulus, psi
-100	760	4.0×10^4
Room Temperature	550	3.3×10^4
700	390	0.8×10^4

Tensile Strength

The tensile strengths of six "dogbone" specimens of 30 pound per cubic foot chemically blown foam were determined according to ASTM Method D651 at -100°F, room temperature and 700°F. Two specimens of the material were tested at each of the three temperature conditions. These tests indicated a wide spread of values. Thus, the individual values as well as the average for the two specimens are recorded in Table XIV.

Table XIV. Tensile Strength of 30 Pound Per Cubic Foot Chemically Blown Foam

Test Temperature, °F	Individual Specimen Test Values, psi		Average Tensile Strength, psi
	Billet No. 1	Billet No. 2	
-100	780	220	500
Room Temperature	770	450	610
700	290	250	270

No tensile strength tests were conducted on the nominal 20 pound per cubic foot foam since it was felt the nature of the material available would have given more widely divergent results than the 30 pound per cubic foot material tested.

Flexural Strength

The flexural strength and modulus of the nominal 20 pound per cubic foot chemically blown foam was determined at -100°F, room temperature and 700°F according to ASTM Method D790. Five specimens were tested at each temperature condition but only those which showed regular behavior were averaged. Some values were low due to localized breaking at sites of unusually large cells, thus it was felt that the test values were not representative of the true material strength. The test values are recorded in Table XV.

Table XV. Flexural Strength and Modulus of 20 Pound Per Cubic Foot Chemically Blown Foam

Test Temperature, °F	Average Flexural Strength, psi	Average Modulus, psi
-100	340	2.4×10^4
Room Temperature	280	2.7×10^4
700	200	0.9×10^4

Conclusions

The volume fraction of continuous voids for the nominal 30 pound per cubic foot chemically blown BTDA-EtOH-DAB foam averaged 0.66, a surprisingly high value since these foams appear to have closed cells. The nominal 20 pound per cubic chemically blown foam has a volume fraction of voids 0.82 indicating a high degree of open cell character while the nominal 40 pound per cubic foot material has a value of 0.38 indicating the relatively low open cell character expected.

The thermal conductivity of the nominal 30 pound per cubic foot chemically blown foams averaged 0.66 BTU/inch/hour/foot^2/°F (2.3×10^{-4} calories/cm/sec/cm^2/°C). This value compares favorably with approximate values of 0.52, 0.58, and 0.92 BTU/inch/hour/foot^2/°F for rigid 25 pound per cubic foot polyurethane foams, 31 pound per cubic foot ABS foams, and 34 pound per cubic foot polyethylene foams.

The compressive strength data indicate that the 30 pound per cubic foot chemically blown foam exhibits its greatest compressive strength in a direction perpendicular to the foaming direction when tested at -100°F and at room temperature. This wide variation in compressive strength, due to the testing direction, is not obvious for the 700°F tests. The same trend just described is generally followed by the compressive moduli data.

The compressive strength and modulus of the nominal 20 pound per cubic foot chemically blown foams tested in the foaming direction generally run about one-third the values of the 30 pound per cubic foot foam tested in the same direction. It is felt that these values can be considerably improved by production of a more uniform cell size foam at the lower densities.

The limited tensile strength data available indicate that the 30 pound per cubic foot chemically blown foams appear to have somewhat similar values at -100°F and room temperature, although the spread of test values tends to make a valid comparison of these few test results suspect. It can be very definitely concluded, however, that the tensile strength drops off rapidly at the 700°F test condition.

6.0 SYNTACTIC FOAMS

The development of syntactic foams is presented in the following sections. The synthesis of the BTDA-EG-DAB resins used to mold the foams is presented in Section 6.1 and the development of the foams described in Section 6.2. The characterization of the finished foams and conclusions resulting from characterization are presented in Section 6.3.

6.1 RESIN SYNTHESIS

The development of the 30 to 60 pound per cubic foot syntactic foams was accomplished with three batches of the tetraester type BTDA-EG-DAB resin. The synthesis of these three resin batches is described in some detail in this section as representative of the resin used in the syntactic foam development program.

Synthesis of Resin Batch D1516-93

A large batch of the BTDA-EG tetraester was produced by adding 2416.8 gm (7.5 mole) of BTDA to 10 liters of hot ethylene glycol and stirring at reflux for 72 hours. The water of reaction was removed by continuous distillation through a heated Vigreaux column. A total of 1330 ml of water-glycol mixture was collected. This water-glycol mixture had a calculated water content of 672 ml which represents 89 ml of water of reaction per mole of BTDA. A 1500 ml quantity of fresh ethylene glycol was added to the product so that the eventual resin produced by reaction with DAB would be at a solids content of approximately 25 percent. The net weight of the ester solution was 13,660.5 gm (1821.4 gm/mole). The carboxyl content of the ester was not determined.

Five 1.5 mole batches of BTDA-EG-DAB resin were synthesized from this tetraester by adding 321.5 gm (1.5 mole) of solid DAB to 2732.1 gm (1.5 mole) of BTDA-EG ester at reflux under argon. The reaction mixtures were refluxed at 180°C to the desired end point viscosities, cooled in an ice bath, and stored under argon. The reaction data for the five individual batches are recorded in Table XVI.

Table XVI. Reaction Data for Resin Batch D1516-93

Batch	Reaction Time, minutes	End Point Viscosity, centipoises
D1516-93A	120	3.3
D1516-93B	140	3.4
D1516-93C	145	3.2
D1516-93D	145	3.3
D1516-93E	145	3.3

A 7.5 mole master batch of BTDA-EG-DAB resin was prepared by mixing the five 1.5 mole batches at room temperature with stirring. The volume of this large batch was approximately 3-1/2 gallons and portions of this resin were used to mold syntactic foams SF-1 through SF-10, as described in Section 6.2.

Synthesis of Resin Batch E1706-19

A master batch of BTDA-EG ester was formed by adding 2416.8 gm of BTDA (7.5 mole) to 10 liters of hot ethylene glycol and heating the reaction mixture to gentle reflux. The mixture was refluxed for 76 hours with continuous removal of water of reaction by means of a heated Vigreaux column. The water removed during the reaction was calculated (from the volume of distillate) to be 79.3 ml water per mole of ester and the resultant ester was found to have a total equivalent percent carboxyl content of 2.1. Approximately 3 liters of fresh ethylene glycol was added to the product so that the resin eventually produced by reaction with DAB would have a solids content of 25 percent.

The E1706-19 resin was prepared from the master batch of BTDA-EG ester as five equal 1.5 mole batches, in the following manner: A 2897.9 gm (1.5 mole) quantity of the BTDA-EG ester was heated to reflux in argon for the first three runs and to 180°C for the last two runs. To each of the heated ester batches, a 321.5 gm

(1.5 mole) quantity of solid DAB was added and the temperature of the reaction mixture brought back to 180°C (after the initial cooling upon the addition of DAB). The reaction mixture temperatures of the first three runs were brought back up to 180°C rapidly by increasing the heat input to the reaction vessel while the last two runs were allowed to reach the 180°C reaction temperature slowly without any increased heat input to the reaction vessel. The reactions were then continued at 180°C until endpoint viscosities in the 3-4 centipoise range were reached and the reaction discontinued. After completion of the five runs, the resin was blended into a master batch designated E1706-19. It was used to mold syntactic foams after the advancement treatments described in Section 6.2.

Synthesis of Resin Batch E1706-20

A master batch of BTDA-EG ester was formed by adding 1750.6 gm (5.43 mole) of BTDA to 8 liters of hot ethylene glycol and heating the reaction mixture to gentle reflux. The mixture was refluxed for 72 hours with continuous removal of water of reaction by means of a heated Vigreaux column. The resultant ester was analyzed and found to have an equivalent unreacted carboxyl content of 5.1. A 5500 ml quantity of fresh ethylene glycol was added to the product so that the resin produced by reaction with DAB would have a solids content of 25 percent.

The E1706-20 resin was prepared from the master batch of BTDA-EG ester as three 1.5 mole batches and one 1.2 mole batch, in the following manner: The 1.5 mole batches were prepared by heating 2958.6 gm (1.5 mole) of BTDA-EG ester to 180° under argon and adding 321.5 gm (1.5 mole) of DAB with stirring. The 1.2 mole batch was made in the same manner, except that 259.8 gm (1.2 mole) of DAB was added to 2340.2 gm (1.2 mole) of the BTDA-EG ester at 180°C under argon.

After completion of the four runs, the resin batches were washed in water and advanced according to the treatment described in Section 6.2.

6.2 FOAM DEVELOPMENT

A series of 25 distinct syntactic foam moldings was prepared in an attempt to develop a void-free, dense, uniform syntactic foam with a nominal density of 60 pounds per cubic foot. All foams were formulated with "3M" brand B35D glass bubbles and BTDA-EG-DAB tetra-ester type resin. The molding parameters used to form these foams are described in the following sections. The physical properties of both the cured and postcured foams are summarized in Table XVII, along with the molding parameters.

After the initial studies to determine the feasibility of producing a syntactic foam from the BTDA-DAB resin systems, it became obvious that the type of resin used and the pressure exerted on the foam formulations were the essential parameters to be considered during the development of the syntactic foam. The type and condition of the resin are important to minimize void formation, while the pressure exerted during molding must be controlled to avoid crushing the glass bubbles.

The initial series of foams were molded to determine the processing conditions necessary to produce dense, uniform, void-free syntactic foams with nominal densities of 60 pounds per cubic foot. The washing, drying and advancement conditions of the resins were varied to reduce void formation and enhance foam uniformity. The charge weight and bubble/resin ratio were varied concurrently in order to bring the finished density of the postcured foams into the 60 pounds per cubic foot density range.

The physical properties and processing parameters of the syntactic foams molded during the development program are summarized in Table XVII. Foams SF-1 through SF-19 laid the groundwork which enabled foams SF-20 through SF-25 to be molded as homogeneous syntactic foams with nominal densities of 60 pounds per cubic foot. Syntactic foams SF-20, SF-21 and SF-22 were machined into the appropriate specimen configurations for the characterization program described in Section 6.3. Foams SF-23, SF-24 and SF-25 were

machined into twenty 2-inch diameter, ten 1-1/2 inch diameter and ten 1 inch diameter test specimens, individually packaged, and shipped to NASA-LRC per contract requirements.

Once the 60 pound per cubic foot density syntactic foam had been developed, efforts were directed towards the development of lower density syntactic foams. An initial series of syntactic foams was molded to determine the most practical lower density range which could be achieved with the BTDA-EG-DAB Pyrrone resin system and the glass bubbles. Various bubble/resin ratios were investigated and the mold charge weight was varied in an attempt to lower the density of the syntactic foams.

This preliminary investigation indicated that the 30 parts by weight bubbles to 70 parts by weight resin ratio produced uniform syntactic foams with densities as low as 30 pounds per cubic foot which retained a high degree of resistance to friability. Efforts to produce foams with much lower densities by means of reducing the mold charge weight or varying the bubble/resin ratio met with failure. Thus, it was concluded that uniform syntactic foams in the 30 to 60 pound density range and with appreciable strength and structural integrity could be consistently and reproducibly molded with the BTDA-EG-DAB resin as currently processed and the glass bubbles. The physical properties and processing parameters of the lower density foams are also summarized in Table XVII.

Syntactic foams with nominal densities of 30, 37-1/2 and 45 pounds per cubic foot were selected for characterization and sample submittal to NASA-LRC. The bulk of the material molded toward this end was of the 30 to 45 pound per cubic foot densities with a limited quantity of 37-1/2 pound per cubic foot density foam molded for sample submittal and limited physical testing.

After development of the 60 and 30 pound per cubic foot density syntactic foams was accomplished, no further difficulties were encountered in molding of the intermediate density foams. Syntactic foams in the density range of 30-45 pounds per cubic foot were molded and machined to the required cylindrical and rectangular sections and a total of 48 specimens submitted to NASA-LRC for evaluation.

Table XVII. Processing Conditions and Physical Properties of Syntatic Foams

Foam Designation	Resin Designation[1]	Resin Preparation Prior to Molding, 2, 3, 4	Bubble/ Resin Ratio, weight percent	Molding Conditions	Mold Charge Weight, grams
SF-1	D1516-93	Vacuum oven at 250°F for 20 minutes	35/65	275° to 500°F in 6-1/2 hours	15.30
SF-2	D1516-93	No treatment	35/65	160° to 300°F in 3 hours	13.00
SF-3	D1516-93	Vacuum oven at 250°F for 20 minutes	35/65	400° to 600°F in 4 hours	13.00
SF-4	D1516-93	Vacuum oven at 250°F for 20 minutes	30/70	300° to 600°F in 6 hours	4.50
SF-5	D1516-93	Vacuum oven at 250°F for 20 minutes	30/70	350° to 600°F in 5 hours	13.00
SF-6	D1516-93	Vacuum oven at 350°F for 10 minutes	30/70	350° to 600°F in 5 hours	15.30
SF-7	D1516-93	Vacuum oven at 350°F for 10 minutes	30/70	350° to 600°F in 5 hours	8.30
SF-8	D1516-93	Vacuum oven at 285°F for 40 minutes and 10 minutes at 340°F	30/70	350° to 600°F in 5 hours	56.60
SF-9	D1516-93	Vacuum oven at 285°F for 40 minutes and 10 minutes at 340°F	30/70	350° to 600°F in 5 hours	56.60
SF-10	D1516-93	Vacuum oven at 285°F for 40 minutes and 10 minutes at 340°F	30/70	350° to 600°F in 5 hours	8.60
SF-11	E1706-19	Vacuum oven at 285°F for 50 minutes and 45 minutes at 335°F	30/70	350° to 600°F in 5 hours	60.00
SF-12	E1706-19	Vacuum oven at 285°F for 50 minutes and 45 minutes at 335°F	30/70	350° to 600°F in 5 hours	60.00
SF-13	E1706-19	Vacuum oven at 285°F for 50 minutes and 45 minutes at 335°F	30/70	350° to 600°F in 5 hours	60.00
SF-14	E1706-19	Vacuum oven from 200° to 300°F in 90 minutes	30/70	300° to 600°F in 6 hours	60.00
SF-15	E1706-19	Vacuum oven from 200° to 300°F in 90 minutes and 10 minutes at 340°F	30/70	300° to 600°F in 6 hours	60.00
SF-16	E1706-19	Vacuum oven from 200° to 300°F in 90 minutes and 10 minutes at 340°F	30/70	300° to 600°F in 6 hours	60.00
SF-17	E1706-19	Vacuum oven at 285°F for 50 minutes, 35 minutes at 335°F and 10 minutes at 350°F	30/70	300° to 600°F in 6 hours	60.00
SF-18	E1706-19	Vacuum oven from 200° to 300°F in 90 minutes and 10 minutes at 340°F	30/70	275° to 600°F in 6-1/2 hours	560.0
SF-19	E1706-19	Vacuum oven at 285°F for 50 minutes 35 minutes at 335°F, 25 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	285° to 600°F in 6-1/2 hours	290.0
SF-20	E1706-19	Vacuum oven at 285°F for 50 minutes, 35 minutes at 335°F, 25 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	285° to 600°F in 6-1/2 hours	275.0
SF-21	E1706-19	Vacuum oven from 200° to 300°F in 90 minutes, 45 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	285° to 600°F in 6-1/2 hours	270.0
SF-22	E1706-19	Vacuum oven from 200° to 300°F in 120 minutes, 50 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	300° to 600°F in 6 hours	1100.0
SF-23	E1706-19	Vacuum oven from 200° to 300°F in 120 minutes, 50 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	300° to 600°F in 6 hours	1135.0
SF-24	E1706-20	Vacuum oven from 160° to 300°F in 150 minutes, 70 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	300° to 600°F in 6 hours	1150.0
SF-25	E1706-20	Vacuum oven from 140° to 300°F in 150 minutes, 35 minutes from 200° to 400°F and held 5 minutes at 400°F	30/70	300° to 600°F in 6 hours	1145.0

Table XVII. Processing Conditions and Physical Properties of Syntactic Foams

Molded Weight, grams	Molded Volume, cubic centimeter	Postcured Weight[5], grams	Postcured Volume, cubic centimeter	Density, pounds per cubic foot		Remarks
				Cured Foam	Postcured Foam	
12.19	11.13	9.90	10.60	68.3	58.3	Large interior voids
10.14	11.34	9.31	10.80	55.8	53.8	Large interior voids
9.53	11.61	9.00	11.06	51.2	50.8	Void free with uniform cell structure
3.31	3.02	3.06	2.88	68.3	66.4	Void free with uniform cell structure
10.73	11.12	10.08	10.59	60.2	59.4	Void free with uniform cell structure
13.58	11.61	--	--	73.0	--	Void free with uniform cell structure
6.88	7.80	--	--	55.0	--	Large interior voids
52.26	53.11	43.10	46.36	61.4	58.0	Shrinkage cracks formed during postcure
44.97	48.72	--	--	57.6	--	Blew apart in the mold
6.37	7.70	--	--	51.6	--	Non-uniform cross-section; hard shell soft interior
40.87	57.96	--	--	44.0	--	Hard exterior shell with interior voids
40.02	44.12	--	--	56.6	--	Many interior voids
53.30	49.42	--	--	67.3	--	Large interior crack
44.63	44.00	--	--	63.3	--	Hard exterior shell with interior voids
47.07	41.55	--	--	70.7	--	Void free with uniform cell structure
47.42	47.34	--	--	62.5	--	Void free with uniform cell structure
46.63	48.01	--	--	60.6	--	Low interior voids but non-uniform resin matrix
448.5	479.2	--	--	58.4	--	Extensive interior voids
239.3	223.9	220.6	215.1	66.7	64.0	Void free with uniform cell structure
225.2	224.8	209.6	216.9	62.5	60.3	Void free with uniform cell structure
223.6	226.9	207.0	216.0	61.5	59.8	Void free with uniform cell structure
893.4	935.4	827.4	887.1	59.6	58.2	Void free with uniform cell structure
927.9	947.6	853.9	895.5	61.1	59.5	Void free with uniform cell structure
935.3	947.4	851.2	891.1	61.6	59.6	Void free with uniform cell structure
932.1	967.8	864.1	921.7	60.1	58.5	Void free with uniform cell structure

Table XVII. Processing Conditions and Physical Properties of Syntactic Foams (Continued)

Foam Designation	Resin Designation[1]	Resin Preparation Prior to Molding, [2,3,4]	Bubble Resin Ratio, weight percent	Molding Conditions	Mold Charge Weight, grams	Density, pounds per cubic foot		Remarks
						Cured Foam	Postcured Foam	
SF-26	E1706-20	Vacuum oven from 160° to 300°F in 150 minutes, 70 minutes from 200° to 400°F, and held 5 minutes at 400°F	45/55	300° to 600°F in 6 hours	5.87	53.0	-	Resists compression but friable
SF-27	E1706-20		45/55	300° to 600°F in 6 hours	5.90	42.0	-	Resists compression but friable
SF-28	E1706-20		45/55	300° to 600°F in 6 hours	6.50	41.0	39.9	Resists compression but friable
SF-29	E1706-20		50/50	300° to 600°F in 6 hours	5.10	36.2	34.4	Resists compression but friable
SF-30	E1706-20		45/55	300° to 600°F in 6 hours	3.50	26.8	-	Broke with manual compression
SF-31	E1706-20		45/55	300° to 600°F in 6 hours	5.70	37.5	-	Resists compression but friable
SF-32	E1706-20		45/55	300° to 600°F in 6 hours	3.80	30.2	-	Broke with manual compression
SF-33	E1706-20		45/55	300° to 600°F in 6 hours	5.30	47.2	46.1	Resists compression but friable
SF-34	E1706-20		45/55	300° to 600°F in 6 hours	4.20	39.1	37.9	Resists compression but friable
SF-35	E1706-20		45/55	300° to 600°F in 6 hours	4.20	37.1	36.4	Resists compression but friable
SF-36	E1706-20		45/55	300° to 600°F in 6 hours	3.80	36.1	35.3	Resists compression but friable
SF-37	E1706-20		40/60	300° to 600°F in 6 hours	3.40	28.4	26.8	Resists compression but friable
SF-38	E1706-20		40/60	300° to 600°F in 6 hours	4.00	38.2	36.1	Resists compression but friable
SF-39	E1706-20		40/60	300° to 600°F in 6 hours	3.60	35.7	33.8	Resists compression but friable
SF-40	E1706-20		35/65	300° to 600°F in 6 hours	3.60	34.1	33.0	Resists compression but friable
SF-41	E1706-27	Vacuum oven from 160° to 300°F in 300 minutes, 240 minutes from 200° to 400°F, and held 5 minutes at 400°F	35/65	300° to 600°F in 6 hours	4.00	40.9	-	Resists compression and abrasion
SF-42	E1706-27		30/70	300° to 600°F in 6 hours	4.40	40.8	39.7	Resists compression and abrasion
SF-43	E1706-27		30/70	300° to 600°F in 6 hours	10.70	48.9	48.0	Resists compression and abrasion
SF-44	E1706-27		30/70	300° to 600°F in 6 hours	10.20	46.2	44.8	Resists compression and abrasion
SF-45	E1706-27		30/70	300° to 600°F in 6 hours	425.0	47.4	45.6	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-46	E1706-27		30/70	300° to 600°F in 6 hours	420.0	46.2	44.6	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-47	E1706-27		30/70	300° to 600°F in 6 hours	420.0	46.2	44.4	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-48	E1706-27		30/70	300° to 600°F in 6 hours	8.00	38.8	37.4	1" (dia) x 1" (high) mold
SF-49	E1706-27		30/70	300° to 600°F in 6 hours	420.0	45.7	44.6	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-50	E1706-27		30/70	300° to 600°F in 6 hours	7.60	34.3	32.7	1" (dia) x 1" (high) mold
SF-51	E1706-27		30/70	300° to 600°F in 6 hours	420.0	45.9	44.6	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-52	E1706-27		30/70	300° to 600°F in 6 hours	420.0	46.0	44.8	Scaled up into 4 1/2" x 6 1/2" x 1" mold
SF-53	E1706-27		15/85	300° to 600°F in 6 hours	8.00	36.1	35.2	Investigation of 30 pound foams
SF-54	E1706-27		10/90	300° to 600°F in 6 hours	8.00	37.0	35.9	Investigation of 30 pound foams
SF-55	E1706-27		30/70	300° to 600°F in 6 hours	8.00	37.4	36.8	Investigation of 30 pound foams
SF-56	E1706-27		30/70	300° to 600°F in 6 hours	6.90	25.8	25.3	Investigation of 30 pound foams
SF-57	E1706-27		30/70	300° to 600°F in 6 hours	7.00	32.3	31.2	Investigation of 30 pound foams
SF-58	E1706-27		30/70	300° to 600°F in 6 hours	213.00	42.8	41.5	Production of 45 pound foams
SF-59	E1706-27		30/70	300° to 600°F in 6 hours	233.00	47.0	45.9	Production of 45 pound foams
SF-60	E1706-27		30/70	300° to 600°F in 6 hours	233.0	46.7	45.6	Production of 45 pound foams

Table XVII. Processing Conditions and Physical Properties of Syntactic Foams (Continued)

Foam Designation	Resin Designation[1]	Resin Preparation Prior to Molding, [2,3,4]	Bubble Resin Ratio, weight percent	Molding Conditions	Mold Charge Weight, grams	Density, pounds per cubic foot		Remarks
						Cured Foam	Postcured Foam	
SF-61	E1706-29	Vacuum oven from 300° to 350°F in 30 minutes, 120 minutes from 350° to 400°F, and held at 400°F for 10 minutes	30/70	300° to 600°F in 6 hours	233.0	43.0	-	Voids due to improperly advanced resin
SF-62	E1706-29		30/70	300° to 600°F in 6 hours	233.0	43.5	-	Voids due to improperly advanced resin
SF-63	E1706-29		30/70	300° to 600°F in 6 hours	247.0	45.7	-	Voids due to improperly advanced resin
SF-64	E1706-29		30/70	300° to 600°F in 6 hours	252.0	46.4	-	Voids due to improperly advanced resin
SF-65	E1706-27 plus E1706-29		30/70	300° to 600°F in 6 hours	238.0	47.5	-	Voids due to improperly advanced resin
SF-66	E1706-29	Vacuum oven from 150° to 300°F in 240 minutes, 120 minutes from 300° to 400°F, and held at 400°F for 5-10 minutes	30/70	300° to 600°F in 6 hours	233.0	46.3	45.2	Production of 45 pound foams
SF-67	E1706-29		30/70	300° to 600°F in 6 hours	238.0	47.9	46.7	Production of 45 pound foams
SF-68	E1706-29		30/70	300° to 600°F in 6 hours	235.5	47.1	45.7	Production of 45 pound foams
SF-69	E1706-29		30/70	300° to 600°F in 6 hours	235.5	47.3	46.1	Production of 45 pound foams
SF-70	E1706-29		10/90	300° to 600°F in 6 hours	7.30	33.2	31.8	Investigation of 30 pound foams
SF-71	E1706-29		10/90	300° to 600°F in 6 hours	323.0	32.8	31.3	Investigation of 30 pound foams
SF-72	E1706-29		30/70	300° to 600°F in 6 hours	50.5	39.2	-	Investigation of 37 1/2 pound foam
SF-73	E1706-29		30/70	300° to 600°F in 6 hours	870.0	46.7	45.6	Scale up to 6 1/2" x 9" x 1" mold
SF-74	E1706-29		30/70	300° to 600°F in 6 hours	725.0	40.1	39.2	Scale up to 6 1/2" x 9" x 1" mold
SF-75	E1706-29		10/90	300° to 600°F in 6 hours	645.0	33.1	31.5	Scale up to 6 1/2" x 9" x 1" mold
SF-76	E1706-29		10/90	300° to 600°F in 6 hours	20.0	33.3	32.4	Specimens for compressive strength
SF-77	E1706-29		30/70	300° to 600°F in 6 hours	24.7	39.5	38.6	Specimens for compressive strength
SF-78	E1706-29		30/70	300° to 600°F in 6 hours	28.5	46.2	45.3	Specimens for compressive strength
SF-79	E1706-29		30/70	300° to 600°F in 6 hours	370.0	36.2	34.9	Production of 37 1/2 pound foam
SF-80	E1706-29		30/70	300° to 600°F in 6 hours	400.0	39.8	38.6	Production of 37 1/2 pound foam
SF-81	E1706-29		30/70	300° to 600°F in 6 hours	400.0	39.9	39.0	Production of 37 1/2 pound foam
SF-82	E1706-29		30/70	300° to 600°F in 6 hours	307.0	30.2	29.2	Production of 30 pound foam
SF-83	--		30/70	300° to 600°F in 6 hours	312.0	30.4	29.5	Production of 30 pound foam
SF-84	--		30/70	300° to 600°F in 6 hours	315.0	30.7	29.7	Production of 30 pound foam
SF-85	--		30/70	300° to 600°F in 6 hours	315.0	31.3	29.5	Production of 30 pound foam
SF-87	--		30/70	300° to 600°F in 6 hours	315.0	30.7	29.4	Production of 30 pound foam
SF-88	--		30/70	300° to 600°F in 6 hours	315.0	31.0	29.9	Production of 30 pound foam
SF-89	--		30/70	300° to 600°F in 6 hours	315.0	29.4	28.4	Production of 30 pound foam
SF-90	--		30/70	300° to 600°F in 6 hours	315.0	31.3	30.3	Production of 30 pound foam
SF-91	--		30/70	300° to 600°F in 6 hours	315.0	30.9	29.9	Production of 30 pound foam
SF-92	--		30/70	300° to 600°F in 6 hours	393.8	31.7	30.6	Production of 30 pound foam

Table XVII. Processing Conditions and Physical Properties of Syntactic Foams (Continued)

Foam Designation	Resin Designation[1]	Resin Preparation Prior to Molding,[2,3,4]	Bubble Resin Ratio, weight percent	Molding Conditions	Mold Charge Weight, grams	Density, pounds per cubic foot		Remarks
						Cured Foam	Postcured Foam	
SF-93	--	Vacuum oven from 150° to 300°F in 240 minutes, 120 minutes from 300° to 400°F, and held at 400° for 5-10 minutes	30/70	300° to 600°F in 6 hours	393.8	31.7	30.6	Production of 30 pound foam
SF-94	--		30/70	300° to 600°F in 6 hours	393.8	32.2	31.1	Production of 30 pound foam
SF-95	--		30/70	300° to 600°F in 6 hours	315.0	31.4	30.3	Production of 30 pound foam
SF-96	--		30/70	300° to 600°F in 6 hours	315.0	30.6	29.6	Production of 30 pound foam

1. All resins used for molding the syntactic foams were of the BTDA-EG-DAB tetraester type.
2. All resins were precipitated and washed in water for 2 minutes except for SF-2 which was washed 4 minutes and SF-6 and SF-7 which were washed 3 minutes.
3. All precipitated and washed resins were dried overnight at 150° to 225°F in a vacuum oven.
4. Resin powders used for foam formulations SF-1 to SF-40 inclusive were ground to pass a No. 80 U.S. Standard Sieve. Remaining resin powders were ground to pass a No. 325 U.S. Standard Sieve.
5. All postcures were from 300° to 700°F in five days under an argon atmosphere.

6.3 FOAM CHARACTERIZATION

The characterization of the syntactic foams involved a continuous evaluation as the development progressed and a final evaluation of the physical properties of the optimized syntactic foam system.

The continuous evaluation of the syntactic foams consisted of visual observation of the sectioned foams and calculations of the "as molded" and postcured densities of these foams. These observations are included in Table XVII. In addition, the volume percent shrinkage of the "as molded" and postcured foams was continually monitored to determine the behavior of the foam formulation under various processing conditions. It was felt that, when predictable foam shrinkage was attained, a more uniform product could be achieved.

Initial shrinkage due to the molding cycle of the syntactic foams varied considerably due to the wide variation of resin treatment and processing conditions. The volume percent shrinkage due to molding for foams SF-1 through SF-18 varied from 5.1 to 18.7 percent. This wide variation in shrinkage was expected in view of the variation in visible void content observed when samples of the unfilled resins were cured under similar conditions. The volume percent shrinkage due to postcure for foams SF-1 through SF-5 was much more consistent, falling between 4.1 and 4.5 percent and averaging 4.4 percent. Foam SF-8 had a volume percent shrinkage of 11.9 percent due to postcure; however this value should not be given much weight because of the extensive cracking of the molded foam.

Foams SF-19 through SF-25 were molded using the processing conditions developed during the molding study of the first eighteen foams. Foam SF-19 was used to determine the proper charge weight necessary, in a large volume mold, to form a uniform, void-free 60 pound per cubic foot syntactic foam. This preliminary foam had an "as molded" density of 66.7 pounds per cubic foot, a postcured density of 64.0 pounds per cubic foot, a volume percent shrinkage due to molding of 15.2 percent, and a volume percent shrinkage due to postcure of 3.3 percent.

Syntactic foams SF-20 through SF-25 had "as molded" densities which varied between 59.6 and 62.5 pounds per cubic foot with an average of 61.1 pounds per cubic foot while the postcured densities varied between 58.2 and 60.3 pounds per cubic foot with an average of 59.3 pounds per cubic foot. The volume percent shrinkage for these six foams due to molding varied between 11.0 and 14.8 percent, with an average of 13.2 percent. The volume percent shrinkage due to postcure varied between 3.0 and 5.2 percent, with an average of 4.3 percent.

Once the behavior of the syntactic foam system was well understood from the 60 and 30 pound per cubic foot foam development programs, the lower density syntactic foams were molded by merely reducing the mold charge weight to a weight calculated to yield the finished foam density desired. Specimens of the various density syntactic foams were taken from the appropriate molded billets and tested for various physical properties as described in the following subsections.

Volume Fraction of Continuous Voids

An attempt was made to determine the volume fraction of continuous voids of one-inch cubes of syntactic foam SF-22 by the epoxy impregnation method described in Section 5.3. Four one-inch cubes were impregnated and the average volume fraction of continuous voids was calculated as 0.23, with individual values ranging from 0.22 to 0.24. However, when the test cubes were sectioned, it became obvious that the foam was so dense that the epoxy resin had penetrated only approximately 1/8 inch of the outer surfaces of the cubes.

To obtain more meaningful values for the continuous void determinations, the specimen configuration was changed from one-inch cubes to thin slabs of 0.2 inch nominal thickness. By reducing the thickness of the 1.0 inch wide by 1.3 inch long slabs, complete impregnation by the epoxy resin was accomplished. The average volume fraction of continuous voids obtained from four such specimens

of the 60 pound per cubic foot foam were found to be 0.36, with individual values ranging from 0.32 to 0.40. It is felt that the latter values for volume fraction of continuous voids are more reliabile because the sectioned specimens showed complete impregnation by the epoxy resin.

The thin slab method was also applied to syntactic foams with nominal densities of 30, 37-1/2 and 45 pounds per cubic foot with values of 0.53, 0.59 and 0.76 volume fraction of impregnatable voids being obtained, respectively.

Specific Heat

The specific heat of 60 pound per cubic foot syntactic foam was determined on specimens of foam SF-22 by the method of mixtures described in Section 5.3. Two runs were made, one on SF-22 foam which had been pelletized into 1/4 inch cubes and one on powdered SF-22 foam.

These BTDA-EG-DAB syntactic foams gave specific heat values of 0.275 calories/gram/°C for the powdered foam and 0.259 calories/gram/°C for the pelletized foam.

The specific heat of a nominal 37-1/2 pound per cubic foot syntactic foam was also determined for 1/4 inch cubes by the method of mixtures. The average value for three determinations on this material was found to be 0.275 calories/gram/°C which closely matches the values obtained for the 60 pound per cubic foot foam. Based upon these determinations, the specific heat for syntactic foam with densities between 30 and 60 pounds per cubic foot can be expected to approximate 0.27 calories/gram/°C in the 8°C to 100°C range.

Thermal Conductivity

The thermal conductivities of three 3 x 3 x 1/8 inch slabs of SF-22 (density, 58 pounds per cubic foot) syntactic foam were determined by the Cenco-Fitch method described in Section 5.3. The individual thermal conductivities of these three slabs were 1.20, 1.50 and 1.91 BTU/inch/hour/foot^2/°F (4.1, 5.2, and 6.6 x 10^{-4} calories/cm/sec/cm^2/°C, which gave an average value of 1.54 BTU/inch/hour/foot^2/°F

(5.3×10^{-4} calories/cm/sec/cm^2/°C. The thermal conductivities of nominal 45 and 30 pound per cubic foot syntactic foams were determined by the same method on two specimens of each type of foam. The average value for the 45 pound per cubic foot syntactic foam was found to be 0.78 BTU/inch/hour/foot^2/°F (2.8×10^{-4} calories/cm/sec/cm^2/°C) and for the 30 pound per cubic foot foam was 0.70 BTU/inch/hour/foot^2/°F (2.4×10^{-4} calories/cm/sec/cm^2/°C).

Compressive Strength and Modulus

The compressive strengths and moduli of 60 pound per cubic foot syntactic foam specimens cut from foam SF-22 were determined at -100°F, room temperature, and 700°F, in accordance with ASTM Method D695. Five 1/2 inch diameter by one inch long specimens of the material were tested at each of the temperatures in the pressing direction and perpendicular to the pressing direction. Most of the specimens exhibited shattering fractures some time during application of the test load. There was no well defined yield point evident from the load deflection curves; thus, no attempt was made to calculate a yield strength and the compressive strength values reported in Table XVIII are "ultimate" values.

The compressive strengths and moduli were also determined for the 30, 37-1/2 and 45 pound per cubic foot syntactic foam according to ASTM Method D1621. This information was obtained on 1 inch x 2 inch x 2 inch blocks of the 30 and 45 pound per cubic foot foams at -100°F, room temperature and 700°F but only at room temperature for the 37-1/2 pound per cubic foot foam due to the limited quantity of material available. The values for these lower density foams are given in Table XIX.

Tensile Strength

The tensile strengths of six "dogbone" specimens of 60 pound per cubic foot syntactic foam specimens were determined according to ASTM Method D651 at -100°F, room temperature, and 700°F. Two specimens of the material were tested at each of the three temperatures.

Table XVIII. Compressive Strength and Modulus of 60 Pound Per Cubic Foot Syntactic Foam

Test Temperature, °F	Average Compressive Strength, psi		Average Modulus, psi	
	Loaded in Pressing Direction	Loaded Perpendicular to Pressing Direction	Loaded in Pressing Direction	Loaded Perpendicular to Pressing Direction
-100	5730	4940	2.0×10^5	2.4×10^5
Room Temperature	4030	3750	2.2×10^5	2.7×10^5
700	3460	3000	6.4×10^4	7.8×10^4

These tests indicated a wide spread of values; thus, the individual values as well as the average of the two specimens are recorded in Table XX. Some of the variation may be the result of obtaining specimens from two different foams (SF-20 and SF-21) of different density. Although the densities of these two billets were very similar (60.3 pounds per cubic foot versus 59.8 pounds per cubic foot), the strength values of specimens from billet SF-20 were consistently higher at all test temperatures. Thus, it is probable that the spread in test data is due to billet-to-billet variation.

Tensile strengths were also determined for 30 and 45 pound per cubic foot syntactic foams according to ASTM Method D651 at -100°F, room temperature and 700°F. Five specimens of the material were tested at each of the three temperatures to give a more reliable average value. The results of these tests are given in Table XXI.

Table XIX. Compressive Strength and Modulus of Lower Density Syntactic Foams

Test Temperature, °F	Average Compressive Strength, psi			Average Modulus, psi		
	30 pound per cubic foot foam	37-1/2 pound per cubic foot foam	45 pound per cubic foot foam	30 pound per cubic foot foam	37-1/2 pound per cubic foot foam	45 pound per cubic foot foam
-100	3230	--	4780	1.7×10^5	--	1.3×10^5
Room Temperature	3150	4230	5970	2.2×10^5	2.9×10^5	2.5×10^5
700	1770	--	3000	1.3×10^5	--	1.6×10^5

Table XX. Tensile Strength of 60 Pound Per Cubic Foot Syntactic Foam

Test Temperature, °F	Individual Specimen Test Values, psi		Average Tensile Strength, psi
	Foam SF-20 Specimens	Foam SF-21 Specimens	
-100	1770	1180	1475
Room Temperature	1610	830	1220
700	1000	570	785

Table XXI. Tensile Strength of Lower Density Syntactic Foams

Test Temperature °F	Average Tensile Strength, psi	
	30 pound per cubic foot foam	45 pound per cubic foot foam
-100	910	1120
Room Temperature	680	1820
700	390	990

Flexural Strength

The flexural strength and modulus were determined for the 30, 37-1/2 and 45 pound per cubic foot syntactic foam according to ASTM Method D790. This information was obtained on 1/4 inch x 1 inch x 5 inch specimens of the 30 and 45 pound per cubic foot foams at -100°F, room temperature and 700°F but only at room temperature for the 37-1/2 pound per cubic foot foam due to the limited quantity of material available. The values for these foams are given in Table XXII.

Table XXII. Flexural Strength and Modulus of Syntactic Foams

Test Temperature, °F	Average Flexural Strength, psi			Average Modulus, psi		
	30 pound per cubic foot foam	37-1/2 pound per cubic foot foam	45 pound per cubic foot foam	30 pound per cubic foot foam	37-1/2 pound per cubic foot foam	45 pound per cubic foot foam
-100	1750	--	2970	2.8×10^5	--	3.8×10^5
Room Temperature	1570	2050	2650	2.6×10^5	3.5×10^5	4.0×10^5
700	1140	--	1690	1.5×10^5	--	2.0×10^5

Shear Strength

The shear strength of the 30 and 45 pound per cubic foot density syntactic foam was determined according to ASTM Method D732 at -100°F, room temperature and 700°F. Five 0.350 inch x 1 inch x 1 inch specimens of each density material were tested at each of the three temperatures described. The results of these tests are given in Table XXIII.

Conclusions

The volume fraction of continuous void determination showed an anomaly which was difficult to explain. The voids increased progressively from the 30 pound through the 45 pound density foams but dropped off to a lower value for the 60 pound density foam. This may be an indication of a high void resin matrix in the lower density foams which is drastically reduced by the tighter packing of the higher density foam. If this effect is not due to inconsistency in specimens it is a property which might be put to good use in ablative applications where reduction of channeling is the desire or on the other hand where a high degree of pregnable voids for filling with a secondary ablator is desired. If this effect is real it is not reflected in the thermal conductivity values, since they progressively decrease with decreasing density without the increased thermal conductivity which would be expected if the voids in the 30 pound density foam are indeed less than those in the

Table XXIII. Shear Strength of Syntactic Foams

Test Temperature °F	Average Shear Strength, psi	
	30 pound per cubic foot foam	45 pound per cubic foot foam
-100	1540	2470
Room Temperature	1400	1900
700	880	1850

45 pound density foam. This effect should be rechecked with another series of foams.

The compressive strengths and modulus values for the syntactic foams reflect the exceptional strength of these materials at both low and high temperatures. The remarkable retention of room temperature values when tested at 700°F indicates the high temperature structural properties which can be expected from these materials. The room temperature strength of the 60 pound foam was somewhat less than would be expected for this density when compared to the lower density foams.

The tensile strength values again reflect the excellent retention of room temperature values when the syntactic foams are tested at 700°F. In all cases the 700°F values are 50 percent or more of the room temperature values. Low temperature tests again reflect the excellent strength of the syntactic foams at -100°F. The tensile strength values for the 60 pound density foam are lower than would be expected. This is again difficult to explain as in the case of room temperature compressive strength values for the 60 pound density foam.

The excellent flexural strength of the syntactic foams is evident when they are compared to the 20 pound per cubic foot chemically blown foams. Although the 30 pound syntactic foams represent a density increase of 50 percent we find the strengths are 5 to 6 times greater than the 20 pound chemically blown foams while the 45 pound density foams show an 8-fold increase in strength for a little more than double the density. Even more remarkable is the retention of strength at elevated temperatures. Both the 30 pound and 45 pound density foams show a retention of two-thirds of their room temperature strength when tested at 700°F.

The shear strengths obtained for the 30 and 45 pound syntactic foams again indicate the excellent strength retention properties of the syntactic foams. The 30 pound foam retains more than two-thirds of its room temperature strength while the 45 pound density foam remarkably indicates very little degradation of shear strength at 700°F.

The physical properties of the 20 and 30 pound per cubic foot chemically blown foams are summarized in comparison with the 30, 37-1/2, 45 and 60 pound per cubic foot syntactic foams in Table XXIV.

Table XXIV. Summary of Pyrrone Foam Properties

Property	Chemically Blown Foam		Syntactic Foam			
	Density, pounds per cubic foot					
	20	30	30	37-1/2	45	60
Compressive Strength (psi)						
-100	760	1720	3230	--	4780	5730
Room Temperature	550	1480	3150	4230	5970	4030
700°F	390	1490	1770	--	3000	3460
Tensile Strength (psi)						
-100	--	500	910	--	1120	1475
Room Temperature	--	610	680	--	1820	1220
700°F	--	270	390	--	990	785
Flexural Strength (psi)						
-100	340	--	1750	--	2970	--
Room Temperature	280	--	1570	2050	2650	--
700°F	200	--	1140	--	1690	--
Shear Strength (psi)						
-100	--	--	1540	--	2470	--
Room Temperature	--	--	1400	--	1900	--
700°F	--	--	880	--	1850	--
Volume Fraction of Continuous Voids	0.82	0.66	0.53	0.59	0.76	0.36
Thermal Conductivity (cal/cm/sec/cm^2/°C)	--	2.3×10^{-4}	2.4×10^{-4}	--	2.8×10^{-4}	5.3×10^{-4}
Specific Heat (8° - 100°C) (cal/gm/°C)	0.25	0.27	--	0.27	--	0.27

7.0 REFERENCES

1. Anon., Chem. Eng. News, 43, 38, May 17, 1965.
2. Bell, V. L., and Pezdirtz, G. F., Polymer Preprints, 6, No. 2, 747, 1965.
3. Bell, V. L., and Pezdirtz, G. F., J. Polymer Sci., B3, 977, 1965.
4. Pezdirtz, G. F., and Bell, V. L., "An Exploratory Study of a New Class of Stepladder and Ladder Polymers - Polyimidazopyrrolones," NASA TN D-3148, 1965.
5. Bell, V. L., and Jewell, R. A., Polymer Preprints, 8, No. 1, 235, 1967.
6. Dawans, F., and Marvel, C.S., J. Polymer Sci., A3, 3549, 1965.
7. Colson, J. G., Michel, R. H., and Paufler, R. M., J. Polymer Sci., 4A-1, 59, 1966.
8. Van Deusen, R. L., J. Polymer Sci., B4, 211, 1966.
9. Van Deusen, R. L., Goins, O. K., and Sicree, A. J., "The Formation and Properties of a Class of Highly Condensed Aromatic - Heterocyclic Polymers," Report No. AFML-TR-66-373, February 1967.
10. Karre, L. E., Keller, L. B., Kimmel, B. G., and Miller, L. J., "Development and Optimization of Pyrrone Polymers," Annual Report on NAS 1-6287, Hughes Aircraft Company, June 1967.
11. Karre, L. E., Keller, L. B., and Miller, L. J., "Development and Processing of Pyrrone Polymers," Final Report on NAS 1-6287, Hughes Aircraft Company, June 1968.
12. "Development of Characterized and Reproducible Syntactic Foam of Phenolic Nylon for Heat Shields." Final Report, Contract NAS 2-2739, December 1965.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546